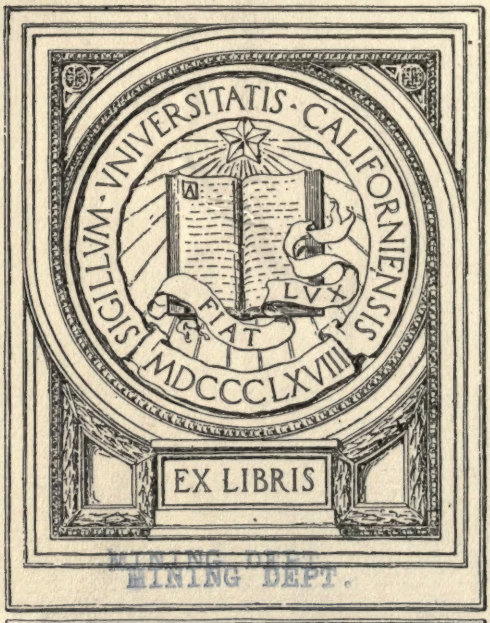
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Jan. 1898.

MANUAL

OF

CHEMICAL TECHNOLOGY

BY

RUDOLF VON WAGNER

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RUDOLF VON WAGNER

TRANSLATED AND EDITED BY

SIR WILLIAM CROOKES, F.R.S.

PAST PRES. C.S., PRES. INST. E.E.

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PREFACE TO THE THIRTEENTH GERMAN EDITION.

In the twelfth edition of this Manual, which appeared in 1886, I confined myself to abridging or totally removing the obsolete matter in the eleventh edition, which had been completed by Wagner shortly before his death, October 4, 1880, and to inserting, or at least referring to, the improvements effected in the last few years.

In the present edition the former arrangement of the subject-matter was rejected, as it seems inadmissible to speak of nitric acid, explosives, and soda before sulphuric acid; to separate cotton from wool, whilst placing in juxtaposition leather, lucifer matches, and milk.

Technology (τεχνη, λόγος)—the doctrine of the industries which improve materials—is divided, for more ready comprehension, into *Mechanical Technology*, which teaches us to modify the *form* of the crude material, and *Chemical Technology*, the task of which is to alter the nature or the composition of the materials. A strict separation of both parts of Technology is impracticable, since Chemical Technology very often requires the help of mechanical arrangements, especially in metallurgy, in the production and elaboration of glass, earthenware, cements, and paper, in tissue-printing, &c. But in the arrangement of the subject-matter in Mechanical Technology the manner in which the form of bodies is modified is exclusively prominent, whilst in Chemical Technology the chemical change of the material is the dominant point of view. The Mechanical Technologist treats, *e.g.*, the cutting of iron, wood, leather, and bread as if in connection; he presupposes the necessary knowledge of the *material*. The Chemical Technologist must pursue the *material* in its various changes, presupposing the mechanical auxiliaries which may be needed (*e.g.*, the various machines for comminution), or they must be treated in such a manner as not to interfere with the survey of the chemical process.

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In every department of Technology fuel is indispensable, and it is therefore discussed in the first place.

If we consider that Germany alone consumes every minute almost a milliard of calories of the heat (or of energy) stored up in the state of fossil fuel, we are justified, whilst no substitute can be thought of, in demanding that more attention shall be paid to fuel than has been hitherto the case.

In Section II. the subdivisions on *Potassium* and *Sodium*, in III. those on *Water*, *Manures*, and *Thermo-chemistry*, are entirely novel; Section I. is chiefly, and Section IV. entirely, new. As compared with the eleventh edition, in that now submitted to the reader more than half the text and also the illustrations will be found new. It is hoped that this new edition will meet with as favourable a reception as its predecessors.

F. FISCHER.

HANOVER, *December* 1888

PREFACE TO THE ENGLISH EDITION.

THE present English version differs so widely from that which appeared in May 1872, that it may be regarded as substantially a new work. It is founded on the thirteenth German edition of 1888, brought out by Dr. Ferdinand Fischer, and re-modelled in accordance with the many important changes which have been recently effected in chemical industry. To these reference has already been made in Dr. Fischer's Preface.

But further modifications have been found necessary. A treatise on *pure* chemistry is of equal value the world over. But a Manual like the present must be in many respects adapted to the conditions of the country where it is written, and, if translated for use elsewhere, it requires modification. The prices of raw materials, of fuel, and of labour have to be kept in view. The laws of different countries interfere with industrial processes in different manners and to a very different extent. Hence certain passages have been omitted as inapplicable to conditions prevailing in Britain, and many notes have been added, for which the Editor considers himself solely responsible.

Bibliographical references to works easily accessible to the English reader are added either in the form of notes or in the text, the latter chiefly under Silver (pp. 187 and 188) and Gold (pp. 189, 190, and 191).

Concerning the illustrations, it may be necessary to add that many of the blocks, instead of being lettered for reference with plain printing characters, are marked in script, and in some cases German words form part of the figures. It has therefore been necessary to add to each such cut an "Explanation of Terms," which the Editor hopes will render it perfectly intelligible to the reader.

Temperatures are almost entirely expressed on the Centigrade scale, the

freezing-point or zero = 0, and the boiling-point of water = 100. Where other scales are used, such as Fahrenheit, they are specially mentioned.

Weights and measures are given according to the metric system.

Specific gravities of liquids heavier than water are generally given on Twaddell's hydrometric scale. This scale has the double advantage over that of Baumé, in that it does not exist in two or more modifications, and that it can be converted into direct specific gravity by a very simple calculation, for which the reader is referred to the tables at the end of the book.

WILLIAM CROOKES.

LONDON, *December* 1891.

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SECTION I.

TECHNOLOGY OF FUEL.

1. FUEL AND ITS TREATMENT.

UNDER fuel we understand those organic substances which, if suitably heated, combine with the oxygen of the atmosphere, evolving light and heat, and forming carbon dioxide and water.* The combustibles chiefly used for generating heat—wood, peat, lignite, and coal (which will be considered separately from the fatty matters and mineral oils, used principally for the production of light)—consist essentially of cellulose, $C_6H_{10}O_5$, and are derived from it as residues richer in carbon, after carbonic acid, water, and methane have been split off, as is shown in the following table, calculated for average specimens free from moisture and ash :—

	Carbon per cent.	Hydrogen per cent.	Oxygen (+ N) per cent.	Heat Value in Thermic Units.†
Wood . . .	49	6	45	4100
Peat . . .	55	5	40	4500
Lignite . . .	66	5	29	5700
Coal . . .	86	4	10	8000
Anthracite . .	94	3	3	8200

Cellulose is formed from carbonic acid and water under the action of the sun's rays—

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2,$$

whilst in the combustion of cellulose—

$$C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O,$$

the same substances are re-constituted with the evolution of 5150 thermic units for each kilo. of cellulose. Exactly the same quantity of heat must have been supplied by the sun's rays for the formation of 1 kilo. cellulose from carbonic acid and water. We therefore consume, not only the heat which is now being yielded by the sun, but the solar heat which has been stored up for thousands of years in vegetable residues (lignite, coal, &c.),—a supply of power, heat, and light which is, without doubt, daily decreasing, and must gradually become exhausted.

This should be a serious warning not to waste fuel, as is now frequently done, or at any rate to attend to its thorough utilisation, so long as we have no other means of producing work, heat, and light in sufficient quantity. The application of water-power for the production of electricity is only a slight attempt in this direction.

The importance, or rather, so far, the necessity of fuel for the whole of our

* This definition excludes chlorine in hydrogen, &c., as also sulphur, phosphorus, and the metals.

† A thermic unit is that quantity of heat which raises 1 kilo. water from 0° to 1°. The mechanical equivalent of heat = 425 kilogrammetres.

industry, and in our latitudes even for human life, justifies a more thorough attention to the utilisation of fuel than it has hitherto generally received.

THERMOMETRY.

History.—The first thermometer is said to have been constructed by Galileo in 1556, but this is disputed, and the invention is currently ascribed to C. Drebble in 1638. It consisted of a globe with a tube welded on, and dipping with its open end into a vessel containing a dilute solution of copper nitrate. Becher (1680) and others improved this air thermometer by taking the pressure of the external air into account. The first spirit thermometer was made about 1640 by Moriani, for the Academy of Florence. Réaumur (1730) also used spirit; Neston (1701), linseed oil; and Fahrenheit of Dantsic (1709) first used mercury. The first metallic thermometer was constructed by Mortimer in 1746. Renaldini (1694) introduced the use of ice and of boiling water for ascertaining the fixed points.

As Fahrenheit's thermometer is still almost exclusively used in Britain and North America and elsewhere, in addition to the scale of Celsius (Centigrade), and that of Réaumur (extensively used in the fermentation industries), it may not be superfluous to remark that these scales may be converted into each other as follows:—

$$F. = {}^{9}/_{4}\,R. + 32 = {}^{9}/_{5}\,C. + 32;$$
$$R. = {}^{4}/_{9}\,(F. - 32); \quad C. = {}^{5}/_{9}\,(F. - 32) = {}^{5}/_{4}\,R.$$

Fahrenheit.	Celsius.	Réaumur (de Luc).	Celsius.	Réaumur (de Luc).	Fahrenheit.	Réaumur (de Luc).	Celsius.	Fahrenheit.
− 20	− 28·88	− 23·11	− 20	− 16·0	− 4·0	− 20	− 25·00	− 13·00
− 10	− 23·33	− 18·66	− 10	− 8·0	+ 14·0	− 10	− 12·00	+ 9·50
0	− 17·77	− 14·22	0	0·0	32·0	0	0·00	32·00
10	− 12·22	− 9·77	+ 10	+ 8·0	50·0	+ 10	+ 12·50	54·50
20	− 6·66	− 5·33	20	16·0	68·0	20	25·00	77·00
30	− 1·11	− 8·00	30	24·0	86·0	30	37·50	99·50
40	+ 4·44	+ 3·55	40	32·0	104·0	40	50·00	122·00
50	10·00	8·00	50	40·0	122·0	50	62·50	144·50
60	15·55	12·44	60	48·0	140·0	60	75·00	167·00
70	21·11	16·88	70	56·0	158·0	70	87·50	189·50
80	26·66	21·33	80	64·0	176·0	80	100·00	212·00
90	32·22	25·77	90	72·0	194·0	90	112·50	234·50
100	37·77	30·22	100	80·0	212·0	100	125·00	257·00
200	93·33	74·66	200	160·0	392·0	200	250·00	482·00

Conspectus of the Ordinary Thermometers.—The numerous instruments devised for measuring temperatures depend on the utilisation of the following phenomena:—

1. Expansion of matter, solid, liquid, or aëriform.
2. Alteration of the state of aggregation.
3. Dissociation; optical and acoustic phenomena.
4. Electric manifestations.
5. Distribution of heat.

1. The expansion of metals has been used, especially for the determination of high temperatures.* All these metal thermometers or pyrometers are untrustworthy.

The most important appliances for measuring heat are the mercurial thermometers. For temperatures from 250° to 350° the space above the mercury should be filled with nitrogen-gas. If this nitrogen is under increased pressure the thermometers can be used up to 400° or even 430°, and are the most accurate and convenient instruments for measuring such temperatures.

Attention must be given to the variability of thermometers which is shown in

* Fischer, *Chemische Technologie der Brennstoffe*, pp. 7 and 313.

two directions. On the one hand, the zero-point, and consequently the entire scale, slowly rises, and on the other the indications after any exposure to a strong heat experience a temporary depression. In these thermometers the transient influence of subsequent heatings is in part marked by the temperature to which the instruments are submitted in their manufacture. In old thermometers this latter effect is weakened. Here there exists between the rise and the fall a relation, in as far as the magnitude of the latter may be regarded to some extent as a standard for the rise to be subsequently expected. To a large extent of this temporary fall there corresponds a large amount of slow rise to be expected in the course of years. A constancy of the indications sufficient for practical purposes can be counted on only if the temporary fall does not exceed a certain limit, which for a heating up to 100° falls distinctly below 0·1°. The magnitude of the fall depends essentially on the chemical nature of the glass. Thermometers of very fusible potash-soda glass are subject to considerable variations, whilst pure potash glass or pure soda glass behaves more satisfactorily, as it has been shown by R. Weber and H. F. Wiebe.* The composition of three kinds of glass (Jena normal glass), made by Abbé and Schott of Jena for mercurial thermometers with an invariable zero, is:—

	I.	II.	III.
SiO_2	67·50	69·00	52·0
Na_2O	14·00	14·00	—
ZnO	7·00	7·00	30·0
CaO	7·00	7·00	—
Al_2O	2·50	1·00	—
BO_3	2·00	2·00	9·0
K_2O	—	—	9·0

Although these thermometers are very decidedly superior to those previously known, an occasional comparison of the zero (crushed ice) and the boiling point of water should be made. For the latter determination attention must be paid to the connection between the boiling-point of water and the atmospheric pressure:—

Barometer.	Boiling-point.
720 millim.	98·49°
730	98·88
740	99·26
750	99·63
760	100·00
770	100·36
780	100·73

Naphthaline and benzophenone are suitable for higher temperatures. The following table gives the boiling-points of naphthaline and benzophenone at various pressures in millimetres of mercury (reduced to 0°):—

Naphthaline.				Benzophenone.			
Temp.	Millimetres.	Temp.	Millimetres.	Temp.	Millimetres.	Temp.	Millimetres.
215·8	722·05	217·2	745·41	303·8	724·77	305·2	746·24
216·0	725·34	217·4	748·80	304·0	727·80	305·4	749·36
216·2	728·45	217·6	752·20	304·2	730·86	305·6	752·47
216·4	731·98	217·8	750·90	304·4	733·92	305·8	755·60
216·6	735·32	218·0	759·02	304·6	736·98	306·0	758·74
216·8	738·67	218·2	762·46	304·8	740·06	306·2	761·90
217·0	742·03	218·4	765·91	305·0	743·14	308·4	765·09

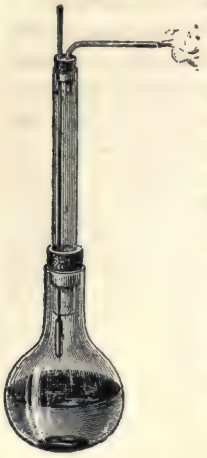
In *determining the boiling-point*,† the direct action of the vapours upon the

* *Jahresber.* 1885, p. 1234.

† *Thermometric Correction for the Projecting Thread.*—If in determination of temperature the mercurial thread is not entirely exposed to the heat in question, the instrument will not give the

thermometer case is to be avoided as far as possible, which is effected by inserting the thermometer in a narrow tube of very thin sheet-metal, closed below (Fig. 1). An enclosure of the entire lower part of the thermometer in such a metal casing, in contact with the atmosphere above, affords the advantage (especially in determinations of boiling-points at reduced pressures that the difference of the pressure existing within and without the thermometer is very much smaller, and that consequently a correction for the influence of the pressure upon the height of the thermometer may be omitted. The compressibility of the glass of the thermometer may be approximately ascertained by determining one and the same temperature with a thermometer in a perpendicular and then in a horizontal position. The difference of the thermometer in these two determinations is caused by the pressure of the mercurial column in the tube upon its case when in an upright position. This effect is the greater the longer the thermometer, and consequently the longer the mercurial column at any given temperature. If the temperatures found by a mercurial thermometer are to be calculated for an air thermometer, the tables of Regnault are no longer available, since different kinds of glass are now in use.

Fig. 1.



Air thermometers * are very accurate, but not well adapted to practical purposes.

2. The determination of high temperatures by the fusion of metals and alloys has been repeatedly attempted. Erhardt and Schertel recommend metal balls of from 100 to 150 milligrams of the following composition :—

Composition.	Melting-point.	Composition.	Melting-point.	Composition.	Melting-point.
per cent.		per cent.		per cent.	
Silver	954°	95Au 5Pt	1100°	65Au 35Pt	1285°
80Ag 20Au	975	90 10	1130	60 40	1320
60 40	995	85 15	1160	55 45	1350
40 60	1020	80 20	1190	50 50	1385
20 80	1045	75 25	1220	45 55	1420
Gold	1075	70 30	1255	Platinum	1775

The more recent determinations of melting-points by Violle are :—

Ir . . .	1950°	Cu . . .	1054°
Pt . . .	1775	Au . . .	1035
Pd . . .	1500	Ag . . .	954

correct indication. If we call the temperature to be determined T, the mean temperature of the mercurial thread, τ, and its length l, the thread, if entirely immersed in the temperature to be measured, will be longer in the proportion $1 : 1 + \alpha (T - \tau)$ if α denotes the co-efficient of expansion of the mercury in the glass. Instead of l the length would be $l + l\alpha (T - \tau)$, or the number of degrees which go to the unit of length being put $= \nu$, then in place of νl in thermometer degrees the length of the thread would be $\nu l + \nu l \alpha (T - \tau)$ or the thermometer, if νl is put $= n$, indicate $n . \alpha (T - \tau)$. If, therefore, we read off on the thermometer the temperature t, the real temperature of the space in question $T = t + n . \alpha (T - \tau)$ or $= \frac{t - n\alpha\tau}{1 - n\alpha}$. The mean co-efficient of expansion of mercury between 0° and 100° being assumed as 0·000181, and that of glass 0·000026, $\alpha = 0{\cdot}000155$. The mean temperature τ of the thread is generally determined by hanging a small thermometer near the middle of the thread, along with the one whose indications are to be corrected, and assuming the temperature of the air read off on the former as the value of τ. On account of the conductivity of the mercurial thread, the value of τ as thus determined is too small, and the calculated value of T is, therefore, too great. For shorter mercurial threads we insert, according to Holtzmann, for compensating this error only 0·000135 instead of α, for long threads the value of τ must be specially determined for each thermometer as just given.

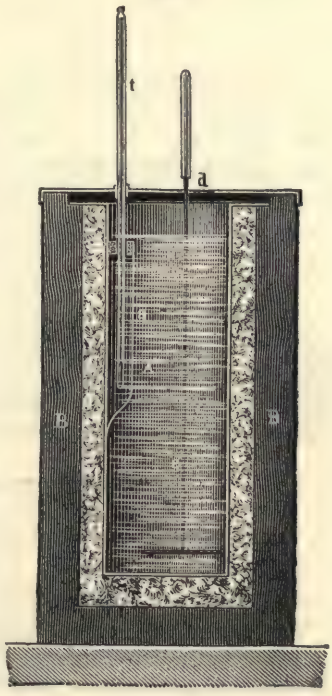
* F. Fischer's *Chem. Technologie der Brennstoffe*, pp. 32 and 319.

For high temperatures H. Seger recommends tetrahedra (normal cones) of mixed glazes composed of felspar, marble, quartz, and Zettlitz kaolin according to the following formulæ :—

No.	Chemical Formula : $0{\cdot}3K_2O, 0{\cdot}7CaO$, and	No.	Chemical Formula : $0{\cdot}3K_2O, 0{\cdot}7CaO$, and
1	$0{\cdot}2Fe_2O_3, 0{\cdot}3Al_2O_3, 4SiO_2$	11	$1{\cdot}2Al_2O_3, 12SiO_2$
2	$0{\cdot}1Fe_2O_3, 0{\cdot}4Al_2O_3, 4SiO_2$	12	$1{\cdot}4Al_2O_3, 14SiO_2$
3	$0{\cdot}05Fe_2O_3, 0{\cdot}45Al_2O_3, 4SiO_2$	13	$1{\cdot}6Al_2O_3, 16SiO_2$
4	$0{\cdot}5Al_2O_3, 4SiO_2$	14	$1{\cdot}8Al_2O_3, 18SiO_2$
5	$0{\cdot}5Al_2O_3, 5SiO_2$	15	$2{\cdot}1Al_2O_3, 21SiO_2$
6	$0{\cdot}6Al_2O_3, 6SiO_2$	16	$2{\cdot}4Al_2O_3, 24SiO_2$
7	$0{\cdot}7Al_2O_3, 7SiO_2$	17	$2{\cdot}7Al_2O_3, 27SiO_2$
8	$0{\cdot}8Al_2O_3, 8SiO_2$	18	$3{\cdot}1Al_2O_3, 31SiO_2$
9	$0{\cdot}9Al_2O_3, 9SiO_2$	19	$3{\cdot}5Al_2O_3, 35SiO_2$
10	$1{\cdot}0Al_2O_3, 10SiO_2$	20	$3{\cdot}9Al_2O_3, 39SiO_2$

The fusion of the cones indicates the temperatures between the melting-point of 90 parts gold and 10 parts of platinum—*i.e.*, about 1145° up to the most intense glow of a porcelain-furnace. If we call the range to be measured 600°, each cone represents a rise of about 30°. It must be remembered that the cones for the higher figures show phenomena of fusion more and more slowly. This is intelligible if we consider that at higher temperatures the heat of the furnace rises more and more slowly on account of the increasing losses of heat. The glazes also become more and more refractory, and sink down less readily. In setting up the cones care must be taken that they always incline to one and the same side, the open side of the form on which the number is impressed, and which almost invariably comes upwards. The cones are to be placed so that the sinking of the point may be observed until it touches the fire-clay plate beneath. The Royal Porcelain Works at Berlin supply 100 cones for 4*s.* 6*d.* The cones act satisfactorily.*

Fig. 2.



3. The determinations of heat depending upon *dissociation*, *optical* and *acoustic* phenomena seem to have no future.†

4. *Electric Thermometers.*—The best of these devices is the electric pyrometer of C. W. Siemens. As the author has satisfied himself by prolonged experiments,‡ it is trustworthy, but it requires very careful manipulation, and is costly (about £25).

5. *Diffusion of Heat.*—Among instruments of this kind§ only the so-called calorimeters are trustworthy. The author‖ recommends the following arrangement as satisfactory :—The cylinder of sheet-copper, A (Fig. 2), 145 mm. high and 50 mm. wide, is suspended in the wooden case, B, which is provided with a convenient handle. The space between the wood and the metal is filled up with asbestos of a long fibro. The apparatus is closed with a thin plate of brass which has a large aperture, *d*, of 20 mm. diameter, for the stirrer, *c*, and for introducing the metal cylinder, and a smaller one for the thermometer, *t*. The normal thermometer with a very small bulb for mercury, ranging from 0° to 50°, is graduated in 0·1°, so that it is possible to estimate 0·01°. It is protected against injury from the stirrer by a strap, *a*, of thin sheet-copper. The stirrer consists of

* *Jahresber.* 1887, p. 30. † *Brennstoffe*, pp. 45 and 326. ‡ *Op. cit.* p. 47.
§ *Op. cit.* pp. 54 and 327. ‖ *Op. cit.* p. 61.

a round disc of copper soldered to a stout copper wire, which is melted into a glass rod, serving as a handle. The copper vessel weighs, *e.g.*, 35·9 grammes, and the stirrer without the glass rod 6·4 grammes; hence the water-value of the calorimeter (specific heat of copper 0·094) with the thermometer 4 grammes. For refrigerating there are used 246 grammes of water, so that the water-value of the calorimeter when full is 250 grammes. For measuring the temperatures the author uses a platinum cylinder weighing 20 grammes, or a cast-iron cylinder of 12 mm. diameter and 20 to 22 mm. in length, weighing 20 grammes, and having two perforations. These cylinders are exposed to the heat, which is to be determined in a small covered iron vessel, secured to an iron rod from ½ to 1 metre in length, and fitted with a wooden handle. They are then brought to the calorimeter and dropped in through the aperture *d*. The metal cylinder falls regularly upon the plate of the stirrer; by moving this up and down, the heat is rapidly and uniformly distributed through the water, so that within a minute the thermometer shows the final temperature. Corrections for evaporation of water or difference of the temperature of the outer air are not necessary. The temperature sought for appears from the following table:—

T.	1 kilo. Water and 1 kilo. Metal $t - t_1$		250 grammes Water and 20 grammes Metal $t - t_1$		Difference per 10°	
	for Iron.	for Platinum.	for Iron.	for Platinum.	for Iron.	for Platinum.
400°	47·4	13·6	3·8	1·09	0·12	0·03
500	62·3	17·4	5·0	1·39	0·13	0·03
600	78·5	21·2	6·3	1·70	0·14	0·03
700	96·2	25·1	7·7	2·01	0·15	0·03
800	115·4	29·2	9·2	2·34	0·17	0·03
900	136·4	33·4	10·9	2·67	0·18	0·04
1000	159·2	37·7	12·7	3·02		

If the thermometer before the introduction of the cylinder marks t_1°, and afterwards t°; and if the increase of temperature is consequently $t - t_1$, the temperature sought for is $= T + t$. If, *e.g.*, the water-value and the calorimeter are 250 grammes water, the temperature of the water $t_1 = 12{\cdot}0°$, and after the introduction of the iron cylinder weighing 20 grammes, $t = 20{\cdot}3°$, then $t - t_1 = 8{\cdot}3°$. The nearest value in the table, 7·7, represents T = 700°; for the remaining 0·6 (8·3 − 7·7) there results 0·6 : 0·15 = 4, *i.e.*, 40°, to which $t = 20$, so that the temperature sought for is 760°. On using a platinum cylinder weighing 20 grammes, let the temperature t_1 be = 15·15, after introducing the cylinder 17·98°, consequently $t - t_1 = 2{\cdot}83°$; 2·67, according to the table, correspond to 900°; to the residue 2·83 − 2·67 = 0·16; and 0·16 : 0·04 = 4, *i.e.*, 40°. Hence the total temperature, 958°.

According to more recent experiments by Pionchon,* the specific heat of iron above 660° is very irregular, so that the platinum cylinder is preferable.

DETERMINATION OF THE VALUE OF FUELS.

The value of fuel employed for the production of heat chiefly depends on the quantity of heat liberated on combustion. Instead of determining this value it is often customary to be satisfied with determining the water, the ash, the sulphur (especially important in alkali works, smelting works, &c.), the nitrogen (especially for obtaining ammonia), further, the carbon and the hydrogen, so that the thermic value may be calculated according to the formula of Dulong (p. 8).

Sampling.—From every load, or every other load, barrow, basket, &c., of the coal as delivered, a spadeful is thrown into a chest fitted with a cover; the coal is then broken up, mixed, and spread out on a level surface in a rectangular shape, and divided into four parts by two diagonal cuttings. Two of these portions lying opposite to each

* *Jahresber.* 1887, p. 33.

other are taken away; the two remaining are again comminuted and mixed until there remains a sample of about 2 kilos., which is put into a closely stoppered bottle. For more careful investigations it is advisable to take in the same manner an average sample of the other half, and to examine it separately. As a loss of moisture is to be feared during the process of sampling, smaller average samples are placed from time to time in weighed test-glasses with glass stoppers to serve for the determination of water.

Samples of peat are taken in a corresponding manner.

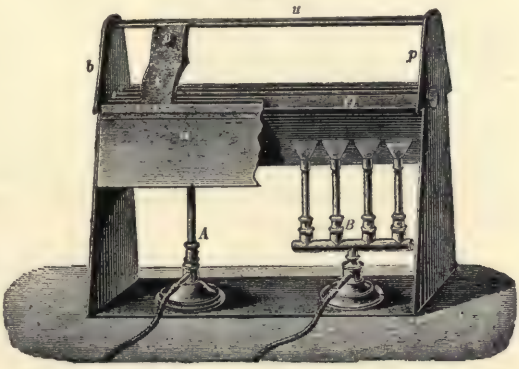
The samples given in to the laboratory must be completely pulverised without rejecting any portions which may be hard to comminute. The determination of moisture must not be effected in open capsules, since many fuels become slowly oxidised if heated in the air. For technical purposes about 20 grammes of the sample are heated for two hours to 105° or 110° in an air-bath either between two watch-glasses or in a crucible with a well-fitting cover, let cool, and weighed. The portion intended for analysis is, if possible, to be allowed to dry in a current of nitrogen, or with the utmost possible exclusion of air.

For the determination of its ash, 5 grammes of the pulverised fuel are incinerated in a platinum capsule. In examining coal, the sample should first stand one or two hours in an open capsule over a small flame, and be heated in a drying closet to about 130°; the incineration is then completed over a flame, which is gradually increased. Coke and anthracite should be very finely powdered.

To determine the yield of coke, from 1·8 to 2 grammes of powdered coal are heated over a Bunsen burner in a platinum crucible with a well-fitting cover (the distance between the mouth of the burner and the bottom of the crucible being 3 centimetres) until flame no longer issues from under the cover.*

For determining the nitrogen by the Kjeldahl process, from 0·5 to 1 gramme of the coal or coke, pulverised as finely as possible (peat does not require pulverising), is boiled for about three hours with 1 gramme mercuric oxide and 20 c.c. of sulphuric acid. When cold there are added 120 c.c. soda-lye, and 1·6 gramme sodium sulphide (in solution), when the ammonia is distilled off and determined volumetrically.

Fig. 3.



For determining carbon and hydrogen, the author uses a simple combustion-furnace (Fig. 3). The two end plates, *b* and *p*, are connected below with the bottom plate, and joined to each other above by the two iron rods, *u*, against which the tiles, *s*, rest above, whilst they stand below in the grooves running along each side. By this means the flames of the burners below, which are screened from currents of air by the

Fig. 4.



metal sheets placed on each side, are compelled completely to enfold the combustion tube as it lies in the open, semi-cylindric channel, *o*. The combustion-tube (Fig. 4), of

* See Fischer, *op. cit.* p. 113.

very refractory glass, open at each end, contains between the two asbestos plugs, *a*, wrapped in very thin platinum foil, a layer, *n*, of granular copper oxide. The platinum boat, *m*, with the sample, is inserted, and the end of the tube *u* is connected with a gas-holder of oxygen, and the other end, *w*, with the calcium-chloride tube, *c*.

When beginning a series of experiments, the combustion-tube is laid in the sheet iron channel, *o*, the tiles are laid against the rods, *u* (Fig. 3), and as the layer of copper oxide is heated to redness by the lamp, *B*, provided with three or four flat burners (for the sake of distinctness the sheet-iron screens are here omitted), whilst a single Bunsen, *A*, burner suffices for the other half of the tube. A current of atmospheric air is drawn through for about ten minutes. The air has passed first through a flask with potassa-lye, and then through another of undiluted sulphuric acid. The tube is then let cool in the current. The stopper, *u*, is then removed, and the sample (about 300 milligrammes), previously dried at 110°, is introduced in the platinum boat, the stopper is again inserted, the calcium-chloride tube, *c*, is connected at the other end, and the combustion is effected as usual in the current of oxygen.

The volatile sulphur is determined in a corresponding manner, but a larger sample is used (0·8 to 1 gramme), and the combustion-tube contains asbestos in place of copper oxide. The sulphurous and sulphuric acids formed are passed into bromiferous potassa-lye and into hydrogen peroxide, and precipitated as barium sulphate.

If the fuel under examination contains *c* per cent. of carbon, *h* per cent. of hydrogen, *s* per cent. of sulphur, *o* per cent. of oxygen, and *w* per cent. of water, 1 kilo. of coal requires carbon $(2{\cdot}667\ c + 8\ h + s - o) : 100$ kilos. or $(2{\cdot}667\ c + 8\ h + s - o) : (100 \,.\, 1{\cdot}43)$ c.c. oxygen or $(2{\cdot}667\ c + 8\ h + s - o) : (21 \,.\, 1{\cdot}43)$ c.c. of atmospheric air for complete combustion. 1 kilo. coal of medium composition consists of—

Carbon	80 per cent.
Hydrogen	4 „
Oxygen	8 „
Nitrogen	1 „
Sulphur	2 „
Water	3 „
Ash	2 „

and requires, therefore, $2{\cdot}667 \,.\, 0{\cdot}8 + 8{\cdot}004 + 0{\cdot}02 - 0{\cdot}08$ or $(2{\cdot}667 \,.\, 80 + 8{\cdot}4 + 2 - 8) : 100 \,.\, 2{\cdot}393$ kilos. or 1·673 c.c. oxygen, or 8 c.c. of atmospheric air.

The thermic value according to Dulong's formula, referred to liquid water at 0° as the product of combustion =

$$\left[8100\ c + 34220\left(h - \frac{o}{8}\right) + 2500\ s\right] :$$

100 heat-units, or referred for convenience to steam at 20° =

$$\left[8100\ c + 28800\left(h - \frac{o}{8}\right) + 2500\ s - 600\ w\right] : 100 \text{ heat-units.}$$

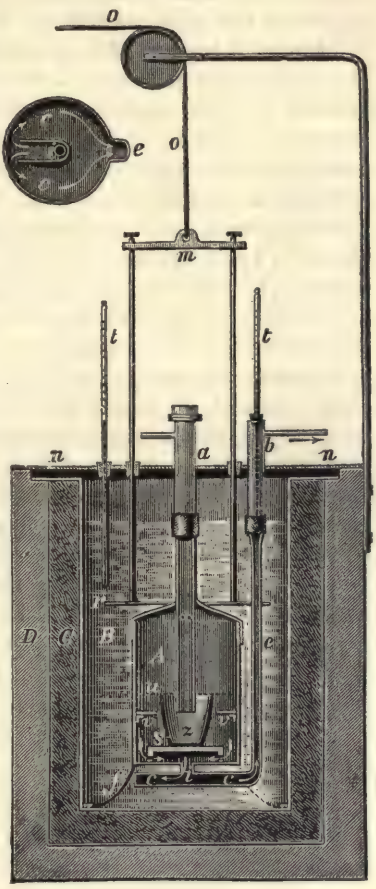
Dulong's formula gives approximately accurate values for wood, peat, and lignite; for coal they are generally from 400 to 800 heat-units too small. Accurate values are obtained only by determining the combustion-value (see p. 9).

In this determination of the combustion-value the author obtained the best possible value by passing the gases evolved in the silver combustion vessel, *A* (Fig. 5), downward through the tube *i* into the flat space, *c*, where, as the transverse section (see accompanying figure) shows, they are compelled in the first place to go to the external side, escaping finally by the flat tube, *e*. The combustion-chamber is secured by the three feet, *f*, to the bottom of the copper refrigerating vessel, which is strongly silvered, by corresponding projections.

The glass pieces, *a* and *b*, are connected with this silver apparatus at the water-level by short caoutchouc pipes. The entrance tube, *a*, for the supply of oxygen, which has

previously been dried, is prolonged by a bent tube of sheet-platinum, which has some small apertures above. The platinum crucible, *z*, can be coated below with asbestos board to prevent too rapid refrigeration, and it is covered with a net of platinum wire, *u*. The gases evolved on the combustion of the sample of coal rise through the platinum sieve, warm the oxygen entering through the tube *a*, mix with it as it enters through the openings in the platinum tube, and are compelled by the annular plate, *v*, to pass again through the hot wire net, *u*, along the glowing side of the crucible, escaping downwards through the aperture, *i*. The refrigeration at the bottom, *c*, and the tube *g* is so complete that the gases escape at the tube *e* scarcely 0·1° higher than the temperature of the refrigerating water. The gases for the determination of water and carbonic acid pass through two calcium-chloride tubes, three sets of potash bulbs, and then, for determining the substances which have not been perfectly burned, through a tube with ignited copper oxide, and again through calcium chloride and soda-lime. The residual oxygen is drawn into a bell gas-holder, and can be used again.

Fig. 5.



The space, *C*, between the silvered copper vessel, *B*, and the wooden case, *D*, is filled with glass-wool. The silvered lid, *n*, consists of two halves, one of which has two semicircular openings for the tubes *a* and *b*, an aperture for the thermometer, *t*, and two for the silvered stirring arrangement, *m*. The thermometer is graduated in $\frac{1}{20}$ degrees, so that 0·01° may be accurately read off by means of a telescope.

In order to decrease as far as possible the communication of heat from the stirrer to it, the two last apertures in the lid are fitted with small ivory inlets, and the two wires which support the disc, *r*, are screwed at top into an ivory support, *m*. To move the stirrer a silk cord, *o*, is passed over a pulley supported by a brass strap (drawn here at one side for the sake of distinctness), so that during an experiment the thermometer may be watched from a short distance by means of a telescope, and the stirrer can be moved at the same time.*

* In order to find the water-value of the apparatus it was completely put together and filled with 1500 grammes water at different temperatures—*e.g.*, temperature of the air, 14·5°; of the water, 20·5°; and of the calorimeter—

Empty	14·64°
Filled, after 2 minutes	20·09
„ 4 „	20·02
„ 6 „	19·97
„ 8 „	19·93
„ 10 „	19·90
„ 12 „	19·86
„ 14 „	19·84

After 6 minutes the temperature was equalised, and then decreased at each reading by 0·03°. In order thus to heat the apparatus from 14·64° to 19·97° the water was cooled down from 20·5° to

With charcoal, peat, &c., no combustible residue remains in the crucible. In order to examine the carbonaceous ash left by coal, the lower part of the crucible is lined with thin sheet-platinum or asbestos paper, which, after the ignition is completed, is introduced with its contents into a combustion-tube, when the combustible parts are converted into carbonic acid and water, which are determined gravimetrically.

A part of the pre-existing water as well as that formed is volatilised in the condensation-tube, and a part escapes as vapour. According as the combustion-value is to be referred to liquid or aëriform water, 610 heat-units must therefore be added or deducted per gramme of water, which seems to have been hitherto neglected. After the combustion is complete, the increase of weight in the calcium-chloride tubes gives the quantity of the aëriform water. The combustion chamber is now, without being previously opened, again connected with the calcium-chloride tubes, carefully heated to about 60°, and dry air is passed through, which carries the watery vapour into the calcium-chloride tubes for weighing.

In carrying out the experiment the calcium-chloride tubes and the potash apparatus are weighed and connected suitably, the coal, which must have been dried at 110° in a current of nitrogen, is weighed off in a covered crucible, which, after its lid has been removed, is rapidly introduced into the dry combustion chamber, *A*, the lid is screwed up, set in the calorimeter vessel, the tube *b* is connected with the absorption-tubes and the tube *a* with the oxygen tube; 1500 grammes water are now poured into the calorimeter vessel, the lid is put on, the stirrer is set in action, and the temperature is read off. In about five minutes from 1 to 1½ litre dry oxygen per minute is allowed to enter. 1 to 2 milligrammes of heavy charcoal splinters, ignited, are thrown in through the tube *a*, and the thermometer is observed with the telescope whilst the agitator is kept in action. If the combustion is completed in four or five minutes the current of gas is moderated. In four to five minutes more the heat is equalised, so that the final temperature may be read off. The absorption-tubes are weighed, and the volatilised water and the residue of the combustion are examined as indicated.

Employed 874 milligrammes coal.

Obtained:

Carbonic acid, 2490 milligrammes, representing carbon		679 milligrammes
Carbonic oxide, 32 „		14 „
Carbon in residue		16 „
		769 „
Water, aëriform, 104 milligrammes „ liquid, 126 „ } = hydrogen		25·5 „
Hydrogen in gases		0·2 „
„ „ residues		0·5 „
		26·2 „

Hence is deduced the following composition of the coal, compared with the ultimate analysis:—

	Calorimeter.		Elementary Analysis.
Carbon	81·12	...	80·91
Hydrogen	3·00	...	3·11
Nitrogen	—	...	0·91
Oxygen	—	...	7·14
Sulphur	—	...	0·51
Ash	7·21	...	7·42

19·97° or 20·03°. The water-value is hence (0·47 × 1500) : 5·33 = 132 heat-units. As the mean of five experiments conducted differently there was found the figure 124. The water-value of the apparatus containing 1500 grammes is therefore 1624 heat-units. According to the author's subsequent experiments, it is preferable to fill the space *C* with eider-down. If the exchange of temperature between the apparatus and the external air is not to be brought into account, its temperature is fixed so much below that of the air as it is higher after the experiment.

The temperature of the air was 14·9°, that of the calorimeter 12·81°; the final temperature reached in nine to ten minutes, 16·86°. Hence we have the following calculation :—

Taken up by calorimeter, 4·05 × 1624 = 6577 heat-units		
For CO, 16 × 2·4 = 77		
„ C, 16 × 8·1 = 130	. .	227 „
„ H, 0·7 × 28·8 = 20		
„ higher specific heat of the products of combustion	. .	20 „
		6824 „

For the water volatilised we must deduct 0·126 × 610 = 77 heat-units; or per gramme coal, 6747 : 0·874 = 7720 heat-units referred to watery vapour at 15° to 20°, whilst Dulong's formula (see p. 8) gives only (81·12 × 8100 + 2·1 × 28800) : 100 = 7175 heat-units. Dulong's formula is consequently useless for mineral coal. With 1·4 per cent. water we have (7720 : 1·014) − (1·4 × 6) = 7605 heat-units. The mean of three experiments gave 7630 heat-units.

The combustion of coal is not quite perfect, but, as the products of combustion are completely determined, and as the combustion-value of carbon monoxide and of hydrogen is accurately known, the inaccuracy which may possibly arise is of the less importance, as any error of moment is completely excluded by a comparison with the elementary analysis. If it is desired to burn also the residue of the coal, this may be effected by directing upon the coal a small hydrogen flame through a narrow platinum tube. Its development of heat can be easily determined with accuracy.*

Wood.—Wood is built up of cells and vessels which consist of cellulose, $C_6H_{10}O_5$ (*see section on* Paper), and contain the vegetable juices. The latter contain, besides water and the ingredients of ash (*see* Potash), various organic matters upon which the composition of the different woods depends. The proportion of water in the different woods is about—

White beech	18·6
Birch	30·8
Cluster oak	34·7
Common oak	35·4
White pine	37·1
Scotch fir	39·7
Red beech	39·7
Alder	41·6
Elm	44·5
Spruce fir	45·2

Air-dried wood contains 12 to 20 per cent. of water. The water diminishes the value of the wood as fuel, not merely by taking up the room of combustible matter, but also by requiring it to be evaporated. The following analyses show the average composition of wood :—

* The objection that such small samples do not represent the true average is ill-founded. In an elementary analysis still smaller quantities are employed. If, as is commonly done, we take from a larger average sample, say of 1 kilo., two specimens of 1 gramme each for the calorimetric determination and for the ultimate analysis, we have, in the agreement of the results, a much better guarantee for accuracy than if we employed 100 grammes for combustion, and were consequently unable to determine the products of combustion and the residues with accuracy, whilst the check of ultimate analysis is also wanting.

	Kind.	Composition dried at 115°.					Air-dry.	
		C.	H.	N.	O.	Ash.	Water.	Value of 1 gramme.*
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	heat-units.
Gottlieb.	Oak	50·22	5·99	0·09	43·42	0·28	13·30	3990
	Ash	49·77	6·26	0·07	43·37	0·53	11·80	4155
	White beech	49·48	6·17	0·06	43·77	0·52	12·02	4161
	Beech, old	49·03	6·06	0·11	44·36	0·44	12·95	4168
	„ young	49·14	6·16	0·09	44·07	0·54	13·95	4101
	Birch	48·88	6·06	0·10	44·67	0·29	11·83	4207
	Pine	50·36	5·92	0·05	43·39	0·28	12·17	4422
	Spruce	50·31	6·20	0·04	43·08	0·37	11·80	4485
Heintz.	Oak	48·94	5·94	—	43·09	2·03		
	Beech	46·02	5·86	—	46·94	1·18		
	Birch	48·89	6·19	—	44·93	0·99		
	Fir, old	49·87	6·09	—	43·41	0·63		
	„ young	50·62	6·27	—	42·58	0·53		

If wood is heated above 150°, it is *de-gasified;* there escape water, carbon dioxide and monoxide, hydrocarbons, then methylic alcohol, acetic acid, &c., whilst the residual charcoal becomes richer in carbon as the temperature rises. Violette on heating wood obtained at—

No.	Temperature of Carbonising.	Composition of the Products (per Cent.).			
		C.	H.	O.	Ash.
1	150°	47·51	6·12	46·29	0·18
2	200°	51·82	3·99	43·96	0·23
3	270°	70·45	4·64	24·19	0·85
4	350°	76·64	4·14	18·44	0·61
5	Melting-point of antimony	81·64	1·96	15·24	1·16
6	„ „ silver	81·97	2·30	14·15	1·60
7	„ „ copper	83·29	1·70	13·79	1·22
8	„ „ gold	88·14	1·41	9·26	1·20
9	„ „ steel	90·81	1·58	6·49	1·15
10	„ „ iron	94·57	0·74	3·84	1·66
11	„ „ platinum	96·52	0·62	0·94	1·94

Samples 1 and 2 are very solid and imperfectly burned, since decomposition only begins at these temperatures. No. 3 is *red charcoal*, which, if produced at this temperature, begins to be friable, and is very readily combustible (300°). No. 4 and all the remainder are *black charcoal*. Nos. 6–10 are very black, dense, solid, and difficult to ignite. No. 11 is so hard that it cannot be easily broken, and if let fall upon stone it gives a metallic sound. It is very sparingly combustible, so that it only begins to burn on direct contact with a flame, and is at once extinguished if taken out of the fire.

MANUFACTURE OF WOOD CHARCOAL.

If the products of distillation are not to be utilised,† the charring is effected in kilns, but otherwise in retorts.

By a kiln we understand a heap of large pieces of wood piled up and covered with earth, or with a mixture of earth and charcoal-dust. The logs of wood are laid either

* Not quite trustworthy.

† The formation of pyroligneous acid during the dry distillation of wood is described by Glauber in his work *Miraculum Mundi*, in 1658. The earliest large charcoal-kilns were set in action in 1819 at Hausach in Baden, but were abandoned shortly after. The increased value of acetic acid and the application of methylic alcohol (discovered by Taylor in 1812 as accompanying wood vinegar) for the production of tar colours have latterly given scope for a more remunerative utilisation of the products of the distillation of wood.

almost at right angles to the axis of the kiln, or horizontally, running out radially from the axis. In the former case the kiln is termed standing, and in the other, lying.

An Italian kiln (Fig. 6) has for an axis a shaft consisting of three or four poles, kept asunder by wedges, *n*, and consists of two or three layers of wood. The conical mass is rounded off by blocks laid horizontally.

A Slavonian kiln (Fig. 7) is distinguished from the last-mentioned by its axis,

Fig. 6.

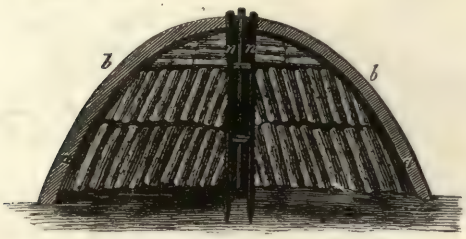


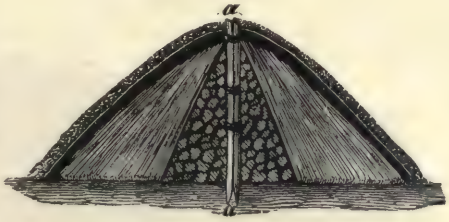
Fig. 7.



which consists of a post driven in, and by the kindling passage, *b*, a channel leading to the axis, by means of which the kiln is set burning.

The Schwarten kiln (Fig. 8), used in Norway, is composed of irregular planks. Three of the largest form the axial shaft, *a*, around which combustible matter is heaped, and conically arranged heaps of the largest wood loppings is superimposed, interspersed with easily combustible matter. This heap forms the nucleus of the kiln, against which the planks are made to lean. The horizontal heaps have the outward appearance of the former, but the blocks of wood are placed horizontally and radially. The axis is either a shaft or a post, with a kindling passage, and the mound, when complete, is covered with a layer of earth.

Fig. 8.

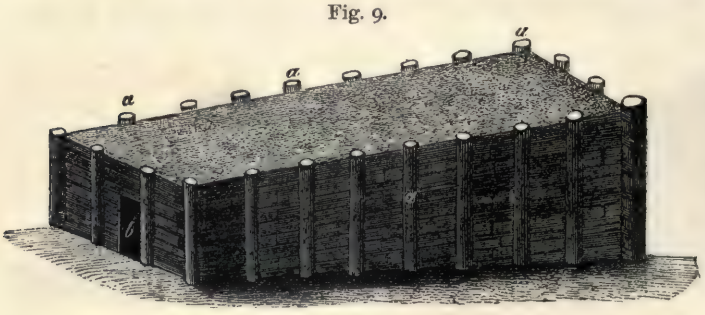


In charcoal-burning we have to distinguish three stages or phases—(1) The sweating; (2) The full combustion; (3) The slow smouldering. The kiln requires a larger supply of air in its interior when first lighted, in order to effect the spreading of the fire, than does one which has been burning for some time. To this end the foot of the heap is at first quite or partially uncovered. As the fire spreads there is evolved watery vapour mixed with products of the dry distillation of wood, which may form, by mingling hydrocarbons with atmospheric air, mixtures resembling detonating gas, and, by explosion, may occasion a partial displacement of the covering, or even a rupture of the heap. By the rapid spread of the fire, by the actual consumption of a part of the wood, and by the decrease of volume due to desiccation and charring, there are produced hollow spaces, which must be carefully filled up. As soon as the vapours escaping at the foot of the mound take a lighter colour comes the stage of slow smouldering. The access of air must be diminished, and for this purpose the mound is covered up wherever it had become open. In about four days the larger portion of the wood is charred. The fire must now be managed so that it spreads from the top downwards, and from the centre towards the circumference. If the smoke from the draught-holes becomes pale and blue, it is a sign of readiness, and the air-holes are closed. When the heap is thus ready in all parts, it is left covered for about twenty-four hours, and let cool whilst protected from the access of air. The mound is then dressed and extinguished.

The carbonisation of wood in heaps for horizontal works is especially practised in

South Germany, Russia, and Sweden. It differs from the process just described, as the wood is gradually charred in portions, whilst the carbonised pieces are at once withdrawn. The site of the kiln is a longish rectangular figure, the front and the back being shorter than the two sides. The heap slopes upwards from the front to the back, and the two sides are both secured by a row of strong perpendicular wooden posts so that the two run parallel. Figs. 9 and 10 show such a heap, Fig. 9 in elevation and Fig. 10 in section. The heap is surrounded with the posts, *a*, and with shingles; it has a covering, *h*, and at the foot a vacant passage, *b*, for kindling. As the fire advances, the charcoal produced at the front is withdrawn, the burner having merely to see that the fire does not spread unequally.

Fig. 9.



Charcoal-ovens may be regarded as permanent walled mounds in which the heat for charring is obtained, exactly as in the common kilns, by the combustion of a part of the wood with sparing access of air. As compared with the kilns with movable coverings, they have the advantage that the pyroligneous acid and the tar can be better and more completely separated. On the other hand, the charcoal obtained is said to be inferior both in quality and quantity to that from the common kilns.

Fig. 10.



Fig. 11 shows one of the simplest kilns; the wood to be charred is heaped up either perpendicularly or horizontally. The wood is introduced either by the aperture, *a*, or the door, *b*. The kindling passage extends from the door to the middle of the sole—*i.e.*, the floor of the kiln. Except a small part of the doorway and of the opening, *a*, all apertures are bricked up, and only re-opened when the charcoal is withdrawn. After the wood has got on fire sufficiently, *b* and *a* are closed. The small openings in the upper part of the oven correspond to the smoke vents in the common kilns. In the charcoal-oven shown in Fig. 12 the two doorways, *a* and *b*, serve for introducing the wood, and *b* is also used for taking out the charcoal. The dampers are at *c*, and the volatile products are carried off to a condenser by the iron pipe, *d*. During the process *a* and *b* are closed. The tar collects chiefly on the floor of the oven and flows into a suitable recipient. Beneath the arched doorway, *b*, there is a small aperture which serves as the entrance to the kindling pas-

Fig. 11.



sage. In the oven Fig. 13 the access of air takes place through the grating, *r*. The wood is introduced through *a* and *b*, and the volatile products escape by the pipe, *q*.

In charring wood in retorts, the wood enclosed in iron or earthenware retorts is heated from without, and arrangements are made for the escape and the complete utilisation of the volatile products. In some cases the production of tar, and in others that

Fig. 12.

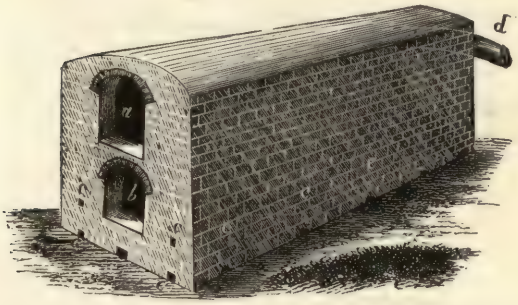
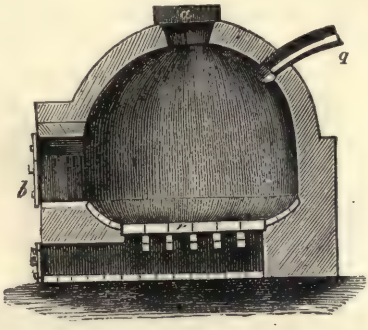


Fig. 13.



of gas, is the chief object. In the tube-furnace the heating and charring of the enclosed mass of wood is effected from within by means of ignited iron tubes, which traverse the furnace, being placed externally in contact with a fire, and opening into a chimney. Instead of passing the hot air and the flame through iron pipes, the wood may be at once charred by the heated air if care be taken that the air and flame are deprived as completely as possible of their oxygen.

If the chief object in charring wood is to obtain tar, a process adopted in Russia may be employed with advantage. According to Hessel's description, the stems and roots of coniferous trees, and preferably of such as are decaying, are chosen, split into pieces, and used for building up the kiln. The site for the kiln (Fig. 14) is funnel-shaped, and provided in its middle with a cavity; the entire surface is coated with clay and covered with roofing shingles, over which the tar flows towards the middle, from whence it passes through a pipe into a vessel placed in a subterranean vault. The wood is piled up in these kilns in six to eight layers, covered with straw or dung, and then with sand or earth.

Fig. 14.



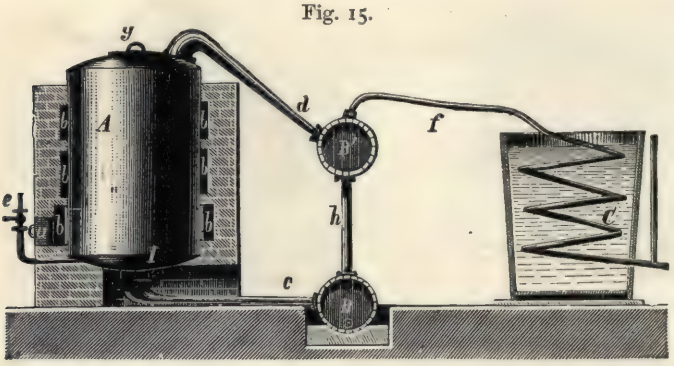
When the kiln has been arranged, it is kindled at forty or fifty openings around its base, which are afterwards choked with sand as soon as the fire has spread upwards through the entire heap. In about six days, during which the filling is kept up continuously, the apex of the heap begins to sink in, and there appears a high, strong flame. In ten to twelve days the removal of the tar begins, and is continued every morning. As this process is simply a slow combustion from without inwards, which is preceded by dry distillation and the formation of tar in the same direction, most of the charcoal is consumed before the process reaches the axis of the kiln.

In Lower Austria (according to Thenius) wood-tar is obtained in a similar manner from such wood of the black fir as yields little or no turpentine. In Bohemia, on

the contrary, there are used woods rich in resin, especially tree-stumps, which contain many particles of resin. In Russia they obtain from 100 parts of wood 17·6 parts of tar and 23·3 of charcoal.

Since 1853 the Swedish so-called "thermo-kettles" have been used in Russia, and deserve to be preferred in every respect to kilns for charring. According to Hessel, such a kettle (Fig. 15) consists of strong sheet-iron, and holds about 8 cubic metres. The charge is introduced through the man-hole, *g*. The heat passes from the fire, *a*, by means of the flues, *b*, round the side walls. To bring the wood rapidly to 100° a current of steam is passed into the kettle through the pipe *e*. The tar, which has already collected in the kettle, runs through the pipe *c* to the store-cask, *B*, whilst the tarry vapours arrive through *d* into the collector, *B'*; what is here condensed descends through *h* to *B*, and what remains as a vapour is liquefied in the condensing apparatus, *C*. The combustible gases, which, however, according to the author's experiments,* have only a low heating value, are led into the fire-box. Besides tar, there are obtained, at the beginning of the distillation, oil of turpentine, pyroligneous acid, and methylic alcohol. The residual charcoal is quenched by means of steam, and taken out through the aperture, *a*. In Germany and England horizontal iron retorts are chiefly used.† (*See also* Methylic Alcohol.)

Fig. 15.



Kind of Wood.	Green.	Summer Dry.	Dried.		Exsiccated.		Charred.		Loss per Cent.								
									Dried.			Exsiccated.			Charred.		
	Specific Gravity.	Specific Gravity.	Specific Gravity.	Loss of Weight. p.c.	Specific Gravity.	Loss of Weight. p.c.	Specific Gravity.	Loss of Weight. p.c.	Central.	Circumference.	Total.	Central.	Circumference.	Total.	Central.	Circumference.	Total.
Oak	1·0745	0·9852	0·804	29·1	0·766	38·2	0·387	76·7	–	3·1	6·1	0·2	6·8	13·3	6·0	17·0	35·2
Ash	0·8785	0·8304	0·771	19·6	0·746	29·1	0·371	77·9	–	4·2	8·4	–	8·6	16·5	7·0	25·0	47·7
Beech	1·0288	0·8160	0·747	33·5	0·700	41·7	0·319	82·3	–	4·3	8·4	–	7·5	14·4	6·5	22·0	43·1
Fir	0·8734	0·7828	0·678	27·6	0·662	37·7	0·351	80·1	–	3·4	6·7	0·2	6·9	13·5	9·0	26·5	50·8
Elm	0·9166	0·7502	0·635	35·5	0·595	42·6	0·284	81·9	0·3	3·4	7·0	0·1	5·9	11·5	9·0	20·0	41·4
Yew	0·9030	0·7106	0·696	24·6	0·642	35·3	0·262	76·2	–	1·1	2·1	0·5	4·3	8·9	10·5	8·0	19·6
Plane	0·9210	0·7044	0·637	33·1	0·604	40·3	0·247	81·4	–	1·7	3·4	–	4·5	8·9	8·5	13·0	30·7
Aspen	0·8809	0·6398	0·515	46·1	0·463	54·0	0·179	86·3	0·4	3·8	7·8	0·3	6·1	12·1	7·0	15·0	32·8
Larch	0·7633	0·6112	0·607	27·3	0·560	34·3	0·238	77·1	0·2	3·4	6·9	0·4	5·2	10·5	8·5	10·5	26·7
White pine	0·8041	0·5878	0·529	37·3	0·510	43·8	0·214	81·0	–	2·3	4·6	0·4	5·7	11·4	10·0	11·0	28·7
Lime	0·7690	0·5810	0·505	41·6	0·484	47·7	0·240	84·1	–	5·7	11·1	0·1	8·8	16·9	8·0	25·5	48·9
Spruce	0·5266	0·4931	0·487	13·1	0·457	23·1	0·193	73·3	–	3·1	6·1	0·3	5·7	11·3	9·0	10·5	27·1

The experiments were made with cubes from the trunks of trees from seventy-five to one hundred years old. For obtaining the wood in the state named "exsiccated" (German *dürr*) the attempt was first made to render the wood chemically dry. As this was a failure, the cubes were placed, at the beginning of May, in the drying-room of a manufactory of inlaid-wood articles at Sulgenbach, near Berne. The results of this

* *Jahresber.* 1880, p. 417. † *Ibid.* 1866, p. 477; 1871, p. 659; 1880, p. 417; 1884, p. 453; 1885 p. 435.

exsiccation, continued for two months at gradually increasing temperatures, which in the last fortnight reached 100°, were at once determined by weight and measure. For charring, the apparatus of the gunpowder works at Worblaufen was employed. The cubes were carbonised in fixed retorts, and, after complete charring and cooling, they were at once weighed and measured.

The yield of different kinds of wood on dry distillation has been determined by Senff,* using a cast-iron retort of 60 centimetres in length and 20 in diameter. The specimens of wood were air-dry. In order to determine the yield on slow and rapid distillation, the retort was either first charged and closed and then submitted to a small fire, or the wood was thrust into the ignited retort, which was then quickly closed and strongly heated. For 4 to 6 kilos. of wood the slow charring took six, and the rapid process only three, hours. When the distillation was complete, the retort remained closed until quite cold. Immediately on opening, the residual charcoal was weighed, and its increase of weight was determined after remaining for several weeks in the air of an ordinary dwelling-room. In the distillate the tar and the crude acid were separated by means of parting funnels, and the quantity of gas was calculated as loss. As the amount of methylic alcohol could not be determined, and as it generally corresponds to that of the pyroligneous acid, the results of experiments are arranged according to the yield of acetic anhydride on slow charring. 100 kilos. of air-dried wood gave the values laid down in the subjoined table; *s* denotes slow, and *r* rapid, action.

Kind of Wood.		Total.	Tar.	Crude Acid.		Anhydride.	Charcoal.		Gas not Condensed.
					Acid.		Total.	Gain.	
		kilos.	kilos.	kilos.	p.c.	kilos.	kilos.	p.c.	kilos.
Carpinus betulus, L. Stem	s	52·40	4·75	47·65	13·50	6·43	25·37	6·09	22·23
	r	48·52	5·55	42·97	12·18	5·23	26 47	10·03	31·01
Rhamnus frangula, L. Peeled shoots	s	52·79	7·58	45·21	13·38	6·05	26·50	5·09	20·71
	r	45·38	5·15	40·23	11·16	4·49	22·53	6·85	32·09
Alnus glutinosa. Stem, peeled	s	50·53	6·39	44·14	13·08	5·77	31·56	6·29	17·91
	r	47·76	7·06	40·70	10·14	4·13	21·11	9·52	31·13
Betula alba, L. Stem	s	51·05	5·46	45·59	12·36	5·63	29·24	1·29	19·71
	r	42·98	3·24	39·74	11·16	4·43	21·46	7·37	35·56
Sorbus aucuparia, L. Stem	s	51·54	7·43	44·11	12·60	5·56	27·84	4·62	20·62
	r	46·40	6·41	39·99	10·41	4·16	20·20	8·72	33·40
Fagus silvatica, L. Stem	s	51·65	5·85	45·80	11·37	5·21	26·69	4·61	21·66
	r	44·35	4·90	39·45	9·78	3·86	21·90	8·45	33·75
Fagus silvatica, L. Branch	s	49·89	4·81	45·08	11·40	5·14	26·19	5·95	23·92
	r	43·14	2·90	40·24	10·89	4·38	21·30	8·99	35·56
Populus tremula, L Stem	s	47·44	6·90	40·54	12·57	5·10	25·47	—	27·09
	r	46·36	6·91	39·45	11·04	4·36	21·33	—	32·31
Quercus robur, L. Stem	s	48·15	3·70	44·45	9·18	4·08	34·68	4·67	17·17
	r	45·24	3·20	42·04	8·19	3·44	27·73	6·36	27·03
Pinus larix, L. Stem	s	51·61	9·30	42·31	6·36	2·69	26·74	8·08	21·65
	r	43·77	5·58	38·19	5·40	2·06	24·06	8·72	32·17
Pinus abies, L. Stem	s	46·92	5·93	40·99	5·61	2·30	34·30	4·82	18·78
	r	46·35	6·20	40·15	4·44	1·78	24·24	9·63	29·41
Pinus abies, L. Branch	s	46·34	8·13	38·21	5·82	2·22	25·55	9·33	28·11
	r	43·85	5·44	38·41	4·20	1·61	23·35	9·93	32·80
Pinus abies, L. Bark	s	40·53	6·99	33·54	3·34	1·12	30·24	—	29·23
	r	37·80	5·36	32·44	2·64	0·86	31·59	—	30·61

The yield of crude acid, tar, and charcoal does not vary essentially in the several kinds of wood, but there is a difference in the percentage of acid in the crude acid, and consequently in the yield of acetic anhydride. The wood of leaf-bearing trees is more productive than that of the conifers; the stem more than the branches, the wood more than the bark, and sound wood more than that which is decayed. Rapid car-

* *Jahresber.* 1885, p. 433.

bonisation produces more gas at the expense of the yield in tar and charcoal, the distillate contains less acid, and the charcoal is more hygroscopic.

PEAT.

Peat * is the product of the spontaneous decomposition (decay) of plants, especially swamp-plants, in many cases mixed with sand, loam, clay, lime, iron pyrites, ochres, &c. Beds of peat are especially formed in places which possess a sufficient temperature for the development of the plants, and standing waters, which during most of the year cut off the peat from contact with the air. The chief swamp and peat plants are: *Eriophorum*, *Erica*, *Calluna*, *Ledum palustre*, *Hypnum*, but above all *Sphagnum*, a plant especially adapted for the production of peat, as it never entirely dies down, but continues growing and ramifying above whilst the lower parts are being converted into peat.

The varying nature of peat depends in part on the different character of the plants from which it is formed, on their more or less complete decomposition, and on the nature of the earthy matter which becomes mixed with the vegetable tissues. The pressure to which the peat is exposed during its formation has also an influence on the density of the mass. According to the difference of the plants from which the peat has been produced we may distinguish (1) bog-peat, consisting principally of species of *Sphagnum;* (2) heath-peat, formed chiefly from the roots and stems of *Erica* and *Calluna;* (3) meadow-peat, formed from grass and sedges; (4) forest- or wood-peat, formed from the wood of trees; (5) sea-peat, formed from sea-weeds.

With reference to its extraction, it is distinguished as spade-peat, which is at once dug out of the bogs in blocks; (2) strained and (3) pressed peat, obtained from paste-like, swampy masses, too soft to admit of digging. If the mass is too liquid, as is sometimes the case in Holland, in Westphalia, and in Northern France, a part of the water is strained off by means of a kind of net. To give the peat more solidity, it is sometimes submitted to pressure in presses of a special construction.

The percentage of water in recent peat is very high; when air-dried, it still retains 15 to 20 per cent. The ash ranges from 2 to 20 per cent.; that with more mineral matter is not worth getting.

The following analyses show the composition of peat:—

Peat from	In 100 parts free from Ash and Dry.				Ash in 100 parts Dry Peat.	Water in Air-dried Peat.	Authority.
	C.	H.	N.	O.			
Kolbermoor	58·51	6·17	0·88	34·44	4·21	15·5	Wagner
Markobach, Rheinpfalz	63·87	6·46	1·60	28·07	2·70	8·0	Walz
Steinwenden, „	58·70	7·04	1·70	32·56	2·04	8·3	„
Vulcaire	60·40	5·96	2·21	31·30	5·58	—	V. Regnault
England	59·84	5·77	2·54	31·85	9·73	25·6	Vaux
Philipstown, light	58·69	6·97	1·45	32·88	—	—	Kane
„ heavy	60·48	6·10	0·88	32·55	—	—	„
Bog of Allen, light	59·92	6·61	1·26	32·21	—	—	Sullivan
„ heavy	61·02	5·77	0·81	32·40	—	—	„

According to Wolff, two samples of peat-ash from the Mark Brandenburg (I. and II.), and according to R. Wagner, an ash from pressed peat from Kolbermoor, in Upper Bavaria (III.), contain—

* BIBLIOGRAPHY: *Torfindustrie und Moorcultur:* E. and K. Birnbaum; Braunschweig, 1880. *Torfwirthschaft Süddeutschland's und Oesterreich's:* A. Hausding; Berlin, 1878. *Torf, Natur und Bedeutung:* A. Vogel; Braunschweig, 1859.

	I.		II.		III.
Lime	15·25	...	20·00	...	18·37
Alumina	20·50	...	47·00	...	45·45
Ferric oxide	5·50	...	7·59	...	7·46
Silica	41·00	...	13·50	...	20·17
Calcium phosphate with gypsum	3·10	...	2·60	...	—
Alkali, phosphoric acid, sulphuric acid, &c.	—	...	—	...	8·55

Uses of Peat.—Peat as obtained in the ordinary manner is a fuel of low value, as it takes up a large space in proportion to its combustive efficacy. This defect is certainly reduced by pressing the peat, but this operation raises the price to such a degree that it can be used only at or near the place of production. The peat charcoal obtained by carbonising in closed receivers has found only a limited consumption, as it is too soft. The dry distillation of peat for the production of paraffine and solar oil can now be scarcely remunerative on account of the diminished price of these products. The same may be said of the proposal to use peat as a source of ammonia. Loose peat finds a limited employment in the manufacture of pasteboards, but it is now extensively used as litter for stables.*

LIGNITE (BROWN COAL, BOVEY COAL).

Lignite is wood modified by decay in contact with water, but the process of decomposition is here much more advanced than in the case of peat. If we look merely to chemical and physical properties, it is not possible to draw a sharp boundary between coal and lignite. The geological and palæontological relations of a deposit supply data for determining these fossil carbons. Every fossil coal which is more recent than the chalk, and is met with in superjacent formations, is termed lignite; every specimen found in formations older than the chalk must be regarded as a true coal. As the proportion of nitrogen in coal is greater than that in lignite, the latter, if heated in a test-tube, yields vapours which have an acid reaction from the predominance of acetic acid. Coal, if similarly treated, yields vapours which have a basic reaction from the presence of ammonia, aniline, lepidine, &c. Another proposed test is to heat the sample in question, finely pulverised, with potassa-lye. Coal leaves the liquid colourless, whilst lignite imparts to it a brown colour owing to the formation of potassium humate (and perhaps also phlobaphen), but we must except the lignites of the northern Alpine tertiaries as soon as they assume the character of fatty coals. According to the experiments of Schinnerer and Morawski (1872) on the action of melting caustic alkalies upon lignite, there is always formed, along with other products, pyrocatechine, probably formed by the decomposition of the phlobaphenes present in the lignite, which, on treatment with a melting alkali, form at first protocatechuic acid and subsequently pyrocatechine.

According to A. Bartoli and G. Papasogli, there are formed, on heating lignite with sodium hypochlorite, carbonic acid, chloroform, oxalic and mellitic acids. Coal is attacked much less readily, and yields no oxalic acid.

According to the degree of decomposition, we distinguish (1) the light-brown fibrous lignite, of the appearance of wood, in which portions of stems, branches, and roots may be plainly recognised (fossil or bituminous wood). (2) Pitch-coal, shining black pieces of a conchoidal fracture, and without any distinctly perceptible trace of woody structure. If the fracture is lustrous, such specimens are known as jet† or, in German,

* Peats containing iron pyrites (sometimes not free from traces of arsenic) cannot be used for litter, as, when subsequently applied to the land, they prove destructive to vegetation. On the same account they are unfit for use in sewage-treatment, the construction of filters for waste waters, &c.—[EDITOR.]

† Jet is the English word for *gagat*, and is derived from the Greek γαγάτες, through the French *jayet, jais*. A peculiarly fine deep-black lignite is found at Whitby and in the Cleveland

gagat. (3) The earthy lignite, a brown mass of decayed pulveriform vegetable matter. It is used as a pigment, Cologne umber. Lignites suitable for the production of solar oil and paraffine are found in Germany (Weissenfels and Zeitz in Prussia, Eschersleben and Saarau in Silesia, Borna in Saxony).

The average composition of the lignites from different localities is :—

Lignites from :	100 parts free from H_2O_3 Ash contain :			100 parts contain Ash.	Authority.
	C.	H.	O + N.		
Gangelsberg, Berlin	63·42	4·18	32·20	8·1	F. Fischer
Braunschweig	71·72	5·76	22·50	7·6	Varrentrapp
Prussian province, Saxony	65·01	6·20	28·77	14·2	Bischoff
Kingdom of Saxony	65·93	6·03	28·03	11·6	Baer
Hessen-Darmstadt	57·63	6·06	36·31	0·6	Liebig
Westerwald	66·35	5·43	28·21	9·3	Casselmann
Regensburg	64·75	5·51	29·72	4·0	„
Hessen, anthracite	81·41	4·44	14·14	7·3	Kühnert
„ ordinary	66·04	5·30	28·65	3·4	„

*

The moisture in freshly raised lignite amounts up to 60 per cent., that of air-dried samples to 15 to 20 per cent. The combustion-value varies with their different composition so greatly that it must be determined in every special case either by elementary analysis and calculation according to Dulong's formula (which only yields approximate results), or by direct determination.

The applicability of lignite is greatly increased by drying and pressing. In order to ascertain the behaviour of lignite on drying, the author dried at 150° a sample of Gangelsberg lignite of the composition stated below as containing 60 per cent. of water. If slowly cooled, spontaneous combustion took place. If air was excluded, the sample, after being heated for one hour each to the following temperatures, had the subjoined composition :—

	110°.	270°.	350°.	450°.	About 1000°.
Carbon	66·34	69·64	74·92	77·98	87·11
Hydrogen	4·34	4·23	3·28	2·69	0·61
Oxygen	23·38	19·25	14·40	11·01	1·36
Nitrogen	0·12	—	—	—	—
Sulphur	0·41	0·21	0·15	trace	—
Ash	5·41	6·67	7·25	8·32	10·92

If treated with superheated steam at 350°, water-gas was formed, *i.e.*, coal was gasified. Drying with superheated steam is, therefore, not to be recommended.

Among the approved systems now in use we may distinguish four—(1) Fire-plate ovens, in which the drying is effected by the products of combustion; (2) Steam ovens, which dry by steam; (3) Hot-air ovens, in which desiccation is effected by heated air; (4) Jacobi ovens, which dry by means of steam and hot air.

Fire-plate ovens were first constructed by Riebeck, of Halle, early in the year 1870. They are now at action in all the briquette factories of Riebeck's mines, and latterly they have been introduced in some new factories. They generally contain fifteen to seventeen round cast-iron plates, of 4 metres in diameter, arranged above each other (Figs. 16 and 17). An axle in the middle of the plates which revolves when the oven is at work supports over each dlate two arms provided with sheet-iron

Hills in England, and in the Departments Aude and Hautes-Alpes. At Aude there existed down to the seventeenth century a guild of makers of jet rosaries (*patenôtriers en jais*). The jet industry existed formerly at Balingen and Gmünd in Würtemberg. At present Whitby is celebrated for the occurrence and the manufacture of jet.

* The lignite of Bovey Heathfield contains, according to Vaux, carbon, 67·9, hydrogen, 5·8, oxygen and nitrogen, 24·8 per cent.—[EDITOR.]

shovels fixed obliquely. On turning this axle the coal is moved and turned over by means of the shovels, and in this manner conveyed over the plates. The shovels are fixed in such a manner that on one plate the lignite is moved from within outwards,

Fig. 16.

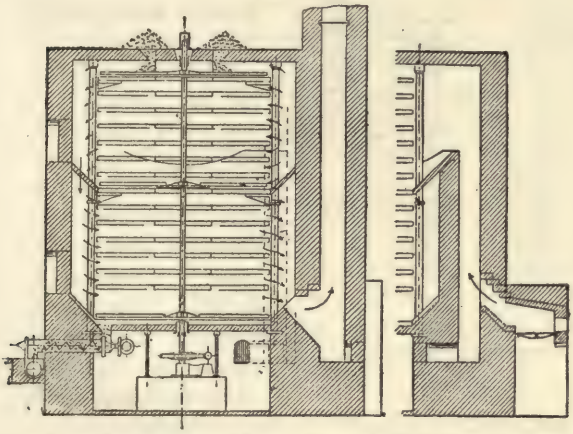
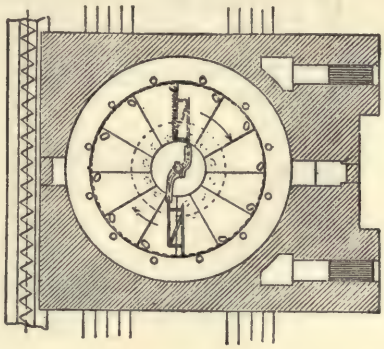


Fig. 17.



and on the next one from the outside inwards. The lignite falls through notches from plate to plate in such a manner that in the plates where the shovels work outwards the fall is at the margins, but in the other plates near the middle. From the last plate the lignite falls through a shoot into the store chest. The plates are in an externally quadrangular furnace of masonry, with a grate in front. The gases of combustion pass up through a channel into the furnace, passing down over the plates and the lignite upon them, and escape at the chimney along with the watery vapour. These ovens are especially adapted for lignites which contain little bitumen for which a high temperature is needed. They have the advantage that the heat can be raised at pleasure, but also the defect that the proper drying of the lignite requires very close attention. Fires and explosions are here more common than with other ovens, and hence they have not been generally adopted. For dusty, adhesive, and smelling lignites they cannot be used.

Of the steam ovens, we mention first the steam-plate oven, similarly arranged to the fire-plate oven, and with the same appliance for moving the lignite. The difference is that the plates stand free in an open space, and that they are hollow and constructed of wrought iron. In drying, the interior of the plates is swept by steam. The plates are supported on four hollow columns, two of which serve to convey steam to and from the plates. The watery vapour escapes by a chimney erected on the oven. A valuable improvement, first devised by Rowold, of Meuselwitz,* consists in inclosing the oven in a sheet-iron case, by which the space in which the oven is set up is kept free from dust and its working can be conveniently watched and regulated. The air and the temperature in the oven-house is thus prevented from becoming unpleasant or hurtful. This oven is suitable for most kinds of lignite, though not for those which need a very high temperature.

The tube drying-oven of Schulz, of Halle (Figs. 18 and 19), is a cylinder in which are a great number of smaller tubes; it is therefore like a tubular boiler. It lies on an incline, and revolves on its longitudinal axle. The axle is formed of two cones, which are contracted towards the middle, where they are connected together. They are hollow, and their covering surfaces are perforated. The steam for drying—exhaust steam from the engines—is let into the upper cone, and, after having steamed through the apertures, it escapes by the lower cone. On the higher front of the apparatus there is a hopper from which the lignite falls into the tubes, gradually works through

* *Jahresber.* 1883, p. 1211.

in consequence of the rotation and the inclined position, and falls out at the lower end. To carry off the condensed steam there are three escape-pipes at the lower end.

Fig. 18.

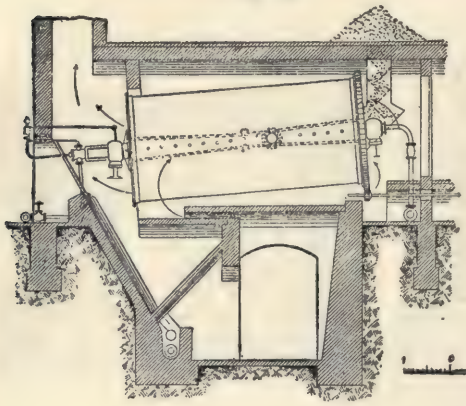
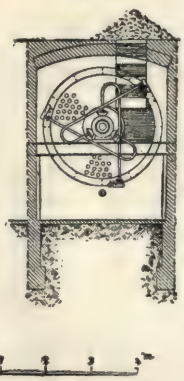


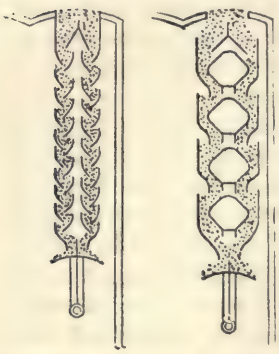
Fig. 19.



This apparatus can boast a simpler motory arrangement than any other. It has been recently set up at Ackermann's works at Bitterfeld, and experience must show if it has further advantages, and what, if any, defects exist. According to Jacobi's view, it is suitable for dusty lignite and such as is of a uniform grain, less suitable for unequal grains, and not at all for adhesive and tumid kinds.

The hot-air oven used in the third system (Fig. 20) consists essentially of sheet-iron plates, arranged like a venetian blind, through which the lignite falls downwards; an arrangement for emptying, consisting of a metal sheet working up and down, effects the gradual transit of the coal. The air for drying is drawn in by ventilators in so-called wind-heaters, *i.e.*, tubular boilers, heated by the spare steam of the engines, and forced through the oven in the opposite direction to the lignite.

Fig. 20. Fig. 21.



At Frose there are twenty-six such ovens, each 4 metres long, 0·5 metre broad, and 5 metres high, which furnish, every twenty-four hours, material for 700 hectokilos. "press-coal." The temperature of the air forced in is on the average 60° to 70°. The oven is easily set in action, and has few moving parts. As defects, must be mentioned the high temperature in the oven-house, the dust, and the irregular drying. For granular lignites, and such as do not need a strong heat, this oven suits well, but not for those which retain a woody texture and swell up or become adhesive.

The fourth system, desiccation by means of steam and hot air, has been evolved from the third, an endeavour being made to remove its imperfections by means of steam-pipes. As appears from Fig. 21, the Jacobi oven is merely a modification of the hot-air oven. Instead of the internal wall of the venetians, there are used pentangular or triangular tubes, by which steam is introduced, to assist in drying the lignite. In addition, hot air is passed in by openings between the tubes. The working and the moving arrangements are the same as in the hot-air oven. In comparison with the latter it has the advantage that the desiccation is more uniform and that a higher temperature can be obtained; in other respects it has the same disadvantages.

All the drying arrangements described have the common grave fault that, in proportion to the cost of installation, they effect far too little work. The manufacture of "press-coal" (dried and compressed lignite) will not receive its full development, involving a suitable utilisation of the deposits of lignite, until this defect is overcome.

An important feature in drying lignite is the collecting space; it is commonly underneath the ovens, or sometimes at one side or over the presses. Here the dried lignite is collected and raised to the presses by means of spirals and elevators. This collecting space has the important function of equalising the differences of the dried lignite arising from variations in the proportion of moisture, different working of the ovens, changes in the temperature of the hot air, &c., since good, marketable press-coals can only be produced with certainty from uniform materials. The lignite goes on drying in this space. It has been unjustly charged with being the source of frequent fires and explosions, and latterly attempts have been made to abolish it. According to experiments at Frose, the subsequent desiccation in this space is essential for the production of good "press-coal." This is intelligible, since the lignite which comes out of the oven at 46°, rises in the collecting-room within eight hours to 70°–75°, the correct temperature for the production of a good article. The fires arise mostly in the ovens and the spirals; a fire in the collecting-room is never formidable, unless the burning material is moved, when it may become dangerous in consequence of explosions. Whether such explosions are due to dust or gas, or both together, is still a matter of dispute. According to Johanni's views we have, in the first place, an explosion of dust, which may lead to a gas explosion if it becomes extensive.

Many kinds of lignite, after desiccation, must be crushed and sifted to yield a good press-coal. This ensures a uniform grain, a further compensation of the temperatures of the single parts, and the elimination of impurities.

The limit of compression of lignite differs according to its texture; it is less when the material is granular and greater when it is dusty. The average is assumed at 45 to 50 per cent. The thickness of press-coals ranges from 30 to 50 millimetres; the transverse section of the smaller is 100 and of the larger 110 square centimetres. The presses make sixty to eighty rotations per minute, and with each one press-coal is produced. The pressure is estimated by Wendland at 1200 to 1500 atmospheres, and a similar value has been found experimentally.

The higher value of press-coal as compared with the original lignite appears from the following figures:—

	Frose Lignite.		Frose Press-coal.
Water	50·0	...	16 per cent.
Combustible	48·5	...	74 „

There are at present in action in Germany 56 press-coal works, with about 142 presses, producing in 1885 about 8 million hectokilos. of press-coal. If we reckon that 4 hectolitres of press-coal are produced by the consumption of 1 hectokilo. of fuel, the manufacture of press-coal—*i.e.*, 32 million hectolitres—consumes about $\frac{1}{10}$th of the German yield of lignite, which is 300 million hectolitres. The value of 1 hectokilo. of press-coal at the spot is on the average 0·8 to 0·9 of a shilling, and the cost of manufacture, material included, 0·6 to 0·7 of a shilling.

COAL.

The great importance of coal-mining appears from the following figures. The quantity raised has increased almost threefold in twenty years. In 1885 Germany raised 58,320,398 tons of coal, of the value of 303 million marks, and 15,355,117 tons of lignite, of the value of 40·4 million marks. This continued increase should prompt the public to a more careful and thorough utilisation of this store of heat and power.

Coal has been formed from lycopods, equisetaceæ, ferns, and other cryptogamous plants. It occurs in the Devonian up to the forest clay, but especially in the carboniferous formation. The most important localities of coal are, in Britain, the Scottish,

the Newcastle, the Lancashire and Staffordshire, the Welsh, and the Cumberland beds. A deposit of coal has recently been discovered in Sussex, but its extent is not yet known. Altogether the coal formation occupies about $\frac{1}{10}$th of the total surface of the British Islands. Ireland is supposed to have possessed at one time very important deposits of coal, which have been chiefly destroyed by denudation. In France the most important coal-beds are those of the Loire, of Valenciennes, of Creusôt and Blanzy, of Aubin, and of Alais. In Belgium the carboniferous districts take up about $\frac{1}{10}$th of the total surface. In Germany there are the palatinate or Saar basins; those of Aachen and Liége, which lie partly in Belgium and partly in Germany; the Westphalian field at Essen, Bochum, and Ibbenbüren; the small beds of Merseberg; the Silesian deposits, extending to Gallicia and Cracow; in Saxony, the beds of Zwickau and the Plauen valley; and in the Bavarian province of Upper Franconia, the field of Stockheim. Austria, with the exception of Bohemia and South Hungary, yields more lignite than coal. The production of coal in Spain, Italy, Russia, and Sweden is unimportant.

In America the coal-fields of the United States are of vast importance. There are three districts; those of Pennsylvania, of Illinois, and the Western fields in Iowa, Nebraska, and Texas occupying a total surface of at least 250,000 square kilometres.

In British North America there are important coal-fields in the provinces of New Brunswick and Nova Scotia, having areas of 8000 square miles. In British Columbia there are also extensive coal deposits, the area of which has not been ascertained. In the island of Trinidad a deposit of coal of superior quality occupies 318 square miles, and is supposed to extend underneath the great pitch lake. The extent of coal in the South American countries has still to be determined.

In South Africa coal is abundant. The British province of Natal contains more coal than Britain ever did, and the fields extend into the Orange Free State.

India contains coal-fields of the area of 3500 square miles. As to the existence of fossil fuel in Burmah we are still in doubt. China is probably richer in coal even than the United States. The coal deposits of Japan and of Yesso are also of considerable importance. The area occupied by the carboniferous system in Australia (Queensland and New South Wales) is estimated at 240,000 square miles.

According to the researches of A. Carnot,* the quality of coal depends not merely on its age and on the circumstances attending its formation, but on the kind of plants from which it has been formed. According to Stein, the behaviour of coal on coking does not depend on its elementary composition.

Scheurer-Kestner—whose results are confirmed by the author—shows that the combustion-value of coal is considerably higher than Dulong's formula requires.

His most recent experiments with coal from Ronchamp (I.), from Altendorf on the Ruhr (II.), and from Glamorgan (III.) gave—

	I.	II.	III.
Carbon	89·09 per cent.	89·92 per cent.	90·27 per cent.
Hydrogen	5·09 „	4·11 „	4·39 „
Nitrogen	1·30 „	1·00 „	0·69
Sulphur	1·03 „	1·00 „	0·49
Oxygen	3·49 „	3·97 „	4·16 „
Value	9130 heat-units	9121 heat-units	8864 heat-units

Schwackhofer obtained the following results for the combustion-value of coal:—

* *Comptes-rendus*, 99, p. 253.

Name of Coal.	C.	H.	O.	N.	H_2O_5.	Ash.	Sulphur.	Heat-units.
Wilczek, Ostrau	77·06	4·50	11·22	0·19	2·91	4·12	0·39	7758
Erzherzog-Albrecht, Ostrau	74·21	4·19	9·82	0·33	3·22	8·23	0·71	7443
Königshütte, Prussia	70·38	4·07	11·85	0·59	8·82	4·29	0·44	6920
Karwiner-Larisch, Ostrau	73·72	4·25	10·39	0·31	3·96	7·37	0·50	7368
Morgenstern, Prussia	61·10	3·17	13·93	0·41	9·07	12·32	0·57	5728
Hermenegilde, Silesia	71·02	4·17	11·46	0·18	2·60	10·57	0·21	6992
Dombrauer, Polnisch-Ostrau	74·69	4·23	12·42	0·07	3·03	5·56	0·50	7280
Carolinen, Prussia	61·42	3·23	13·64	0·24	7·29	14·18	0·78	5758
Glückshilf I., Waldenburg	70·50	3·94	9·28	0·19	1·60	14·49	0·63	6955
Jaklowetz, Silesia	72·59	3·90	10·08	0·20	2·40	10·83	0·35	7044
Waterloo, Prussia	69·70	3·74	13·60	0·40	6·28	6·28	0·40	6571

Anthracite occurs chiefly in transition formations, especially between the strata of clay-slate and of grey-wacke and between mica-slate and the beds by which it is intersected. It is deep black, brittle, of conchoidal or irregular fracture, burns with a feebly luminous but smokeless flame, does not soften in the fire, but often crackles and decrepitates. Jacquelain obtained the following results on the analysis of certain anthracites :—

From	C.	H.	O.	N.	Ash.
Swansea	90·58	3·60	3·81	0·29	1·72
Sablé	87·22	2·49	1·08	2·31	6·90
Vizille	94·09	1·85	1·08	2·85	1·99
Isère-Dep.	94·00	1·49	1·08	0·58	4·00

Anthracite owes its superiority to other fuel to its cleanliness, hardness, and its smokeless combustion. In Swansea and in some of the Eastern American States, especially along the river Lehigh in Pennsylvania, it has been used since 1839 for the reduction of iron ores in blast furnaces. It serves also in lime-burning, brick-burning, in salt works, and as a domestic fuel. Since 1875 the attempt has been made to convert anthracite into coke by breaking it up previously along with caking coal and coke.

Boghead Coal, or Torbane Hill mineral, is found near Bathgate, at Rocksoles near Airdrie, at Pirnie, Capeldrea, Kirkness, and Wemyss in Fife. The Torbane Hill coal, famous for the unedifying litigation as to its nature, is considered the most valuable coal known for gas-making. It is amorphous, with a conchoidal fracture, and contains impressions of the stems and roots of *Sigillaria*. It yields a coke of little value, and on dry distillation it gives off paraffine, photogene, and solar oil, whilst true coal produces anthracene, naphthaline, and benzene.

Its composition, according to Dr. Stenhouse, F.R.S., is—

Carbon	65·72
Hydrogen	9·03
Nitrogen	0·72
Oxygen	4·78
Ash	19·75
	100·00

The ash of Torbane Hill coal is stated by the same authority to contain—

Silica	58·31
Alumina	33·65
Ferric oxide	7·00
Potash	0·84
Soda	0·41
Lime and sulphuric acid	traces

Boghead coal is used both as fuel for the manufacture of gas, and for the pro-

duction of paraffine and lubricating oils. Other forms of brown cannels approximating to the original Torbane Hill deposit, which is now nearly exhausted, are found at Wemyss, at Rigside and near Lesmahagow in Lanark.

Hilt classifies coals according to their yield of coke, which ranges from 52 to over 90 per cent.

L. Gruner maintains that the technical value of a coal can be better ascertained by proximate than by ultimate analysis. He distils the coal in a retort and incinerates the residue. In true coals the combustion-value generally coincides with the quantity of fixed carbon left after distillation; this is less commonly the case with anthracites and lignites. He distinguishes five kinds of coal—(1) dry coal, with a long flame, yielding 50 to 60 per cent. of coke, which is powdery or at most fritted; (2) fat or gas coal, with a long flame, yielding 60 to 68 per cent. of coke, fused and tumid; (3) smithy coal, giving 68 to 74 per cent. of coke, fused and of mean density; (4) coking coal, with a short flame, yielding 74 to 82 per cent. of a very compact coke with few blisters; (5) anthracites, giving 82 to 90 per cent. of a fritted or powdery coke.

The following analyses of the ash of Upper Silesian coals are taken from E. Jensch :—

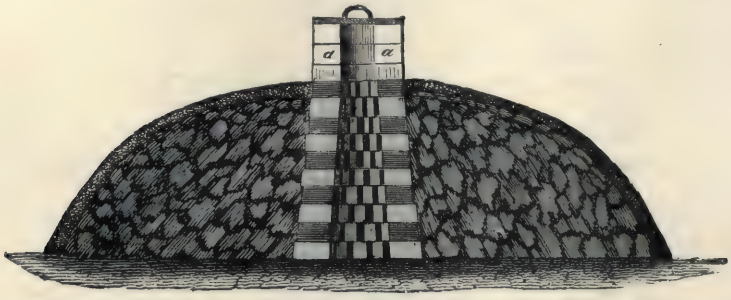
	1.	2.	3.	4.	5.	6.
Sand, SiO_2 (soluble)	39·450	26·070	3·860 20·940	6·890 38·340	6·430 28·200	9·200 27·450
Al_2O_3	18·230	27·800	20·630	15·840	23·820	28·570
Fe_2O_3	15·680	19·840	26·020	19·270	18·580	10·760
MnO	1·330	0·420	2·840	1·170	1·430	0·200
ZnO	0·260	0·370	1·120	0·090	0·550	0·860
PbO	0·021	0·069	0·058	0·037	0·082	0·056
CdO	0·008	0·001	0·003	0·005	0·004	0·002
CaO	6·020	11·150	6·400	2·160	3·290	7·450
MgO	2·440	4·210	4·690	0·810	0·870	2·000
Alkalies	2·170	0·760	2·980	2·100	3·090	2·090
SO_3 (total)	12·830	7·380	9·480	11·840	12·610	10·880
P_2O_5	1·290	1·480	0·850	1·090	0·970	0·230

The presence of copper is to be ascertained in coals used in iron smelting. Schulze* detected thallium and lithium in coal.

Coke.—The object of the coking of coal is (1) to increase the proportion of carbon and thus to obtain a higher temperature; (2) to expel evil-smelling constituents (especially for household consumption); (3) to deprive coal of the property of caking together, whereby the due access of air is hindered, especially in blast furnaces; (4) to expel a part of the sulphur always present in the form of iron sulphide.

Coking in heaps is very similar to charcoal-burning. On the spot selected there is

Fig. 22.



built a chimney shaft from 1 to 1½ metre in height, which serves for the axis of the heap. It is 0·3 metre in diameter, and is provided with several rows of air-holes, by

* *Jahresber.* 1886, p. 1069.

which it is kept in connection with the heap of coal. The largest pieces of coal are laid round the chimney and smaller pieces towards the circumference so as to round off the heap (Fig. 22). The intervals between the lumps are filled up with small coal. At the sole of the heap there are formed channels or air passages leading from the circumference towards the shaft. At the bottom of the shaft there are laid dry chips of wood, which are kindled from above. The heap is fired as long as smoke is given off, the top of the chimney is then closed with an iron cover, and the mouths of the air-channels are choked with earth. Sometimes cooling is promoted by the application of cold water, which is erroneously thought to desulphurise the coke. The whole process is very similar to charcoal-burning.

Oven-coking.—At present coking is effected almost exclusively in special furnaces, coke-ovens, in which the management of the fire is easier, an excessive consumption of the coal is more readily avoided, and the yield is in general greater. The ovens in greatest use are that of Appolt, which may be regarded as a kind of upright gas retort with openings for the escape of the gases, and latterly the Coppée oven.

Of the closed coke-ovens of earlier construction may be mentioned one used at the ironworks at Gleiwitz in Silesia, shown in section in Fig. 23. The cylindrical coke-room, *A*, with a perforated arch above, is provided with register-openings in the walls, *o*, which can be closed from without by means of plugs. There are also similar apertures in the sole, forming a kind of grate. But the sole may be advantageously constructed solid if care be taken that the lowest row of apertures is placed immediately above the sole. The coal to be coked is introduced partly through the opening, *b*, in the arch, and partly through the door, *a*. First the larger pieces are inserted, though a passage opening at the door is left free for the introduction of burning coals. After the oven is filled up to the lower part of the discharge-pipe, *r*, the door is bricked up to the mouth of the kindling passage, all the register-openings are closed except the lowest row, and the opening of the arch is closed with the iron cover, *d*. As soon as the coals display an average redness through the register-holes of the lowest row, these are closed and the next row is opened, which is the case in about ten hours; after another ten hours, the second row is closed; after sixteen hours, the third; and after a further three hours, the fourth. The oven, when entirely closed, is let stand twelve hours to cool; the door, *t*, is then opened, the glowing cokes are drawn out with a hook and at once extinguished with water. The above furnace takes 2 tons of coal, and, on an average of several months, it yields 53 per cent. of coke by weight or 74 by volume. The gases and vapours escape through the pipe, *r*, to a condensing apparatus which serves for two adjacent ovens. It liquefies and receives the tarry vapours, letting the gases escape.

Fig. 23.

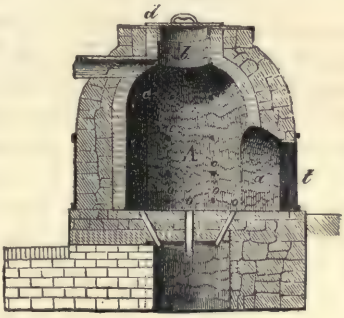
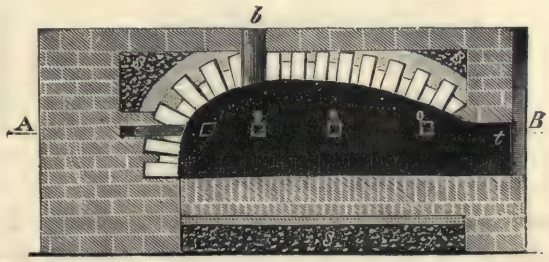


Fig. 24.

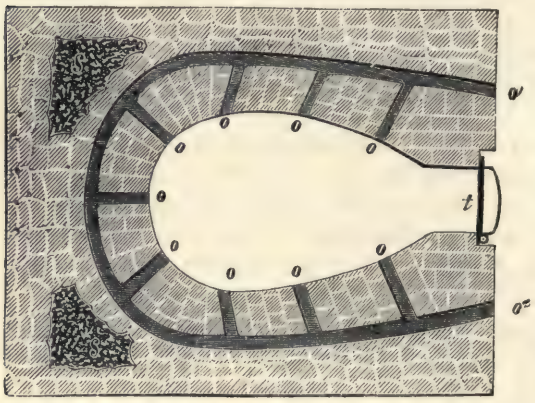


The coking of small coal is effected on hearths arched over after the manner of a baker's oven. The waste of the coal mines may be very advantageously utilised by

coking, since the particles, when heated, cake together and yield as firm coke as does lump coal.

In the coke-works on the Saar and at Sulzbach, as well as formerly in some iron-works in Lorraine, ovens are employed as shown in section, Fig. 24 (p. 27), and, Fig. 25, in ground plan. They are advantageously distinguished from the earlier coke-ovens (in which the access of air took place through chinks in the doors and the chimney) by the circumstance that a regular current of air takes place through openings in the vault. The sole of the oven is egg-shaped; the length is 3 metres, the breadth 2, the greatest internal height 1 metre. The chimney, $1\frac{3}{4}$ metre high, serves for introducing the small coal. A peculiarity in this furnace is the distribution of the air-supply. At the height of 0·3 metre above the sole there runs a draught channel of horseshoe shape round the oven space, and opens at *o'* on each side of the door, *t*. The air streaming into these openings is distributed through nine cross-channels, *o*, and rushes into the oven space. The door, *t*, closes the opening almost perfectly. A charge of 1 to $1\frac{1}{4}$ cubic metre of small coal is coked in this oven in twenty-four to thirty hours.

Fig. 25.



Coke-oven of Appolt Bros.—The first of these ovens was erected, in 1855, at St. Avold (German Lorraine). It is distinguished by the form of its standing shaft, which is heated from without, whilst the heating of the oven shaft is effected merely by vapours

Fig. 26.

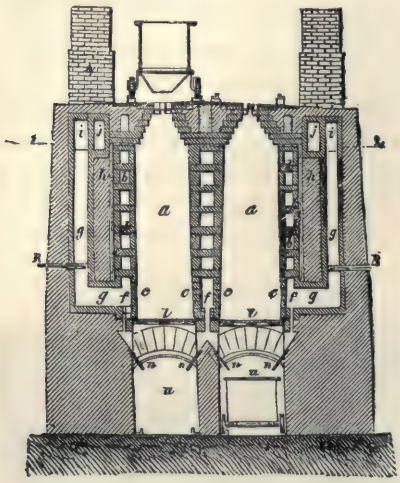
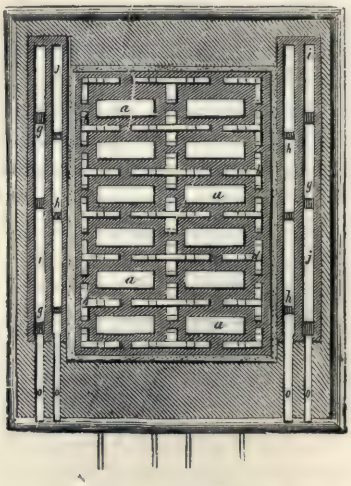


Fig. 27.



and gases evolved and ignited during the coking. Fig. 26 shows the section, and Fig. 27 a horizontal section on the line 1 to 2. In order that the heat may pass better into the shafts, *a*, they are of a prolonged quadrangular section (0·45 and 1·24 metre by 4 metres deep); and, the better to utilise the heat, every twelve shafts are united in two rows to a general oven. The several shafts (whose walls are separated by hollow spaces, *b*)

are connected with each other and with the mantle by masonry; the empty spaces are also connected with each other. Each compartment has two apertures—an upper one by which the coal is introduced, and a lower through which the cokes are allowed to drop out. In the lower part of the side wall of the compartments there are left between the stones narrow slits, *e*, through which pass the gases and vapours, which are burnt in the hollow spaces with the co-operation of the air which enters through *b*. The heat thus generated effects the coking of the coal in the interior of the compartments.

The products of combustion escape through the channels *g* and *h*. The draught is regulated by the slide, *R*. The channels *g* vent into a horizontal channel, *i*, and the channels *h* into *j*. The two channels *i* and *j* unite in the flue, *k*. The compartments of the oven (Fig. 26) are contracted at their upper end by projecting stones, so that there remains only a small opening, which is closed with an iron cover. This cover has in the middle a pipe, through which a part of the gaseous and vaporous products of distillation can be led off. A tramway running along over every series of oven compartments receives the truck, which each time brings to a compartment its charge of 1200 kilos. of coal. In the solid masonry below the oven there are two passages, in which the trucks for receiving the coke travel on tram-lines.

In working the oven, wood fires are placed in the compartments, upon which coal is then placed. The interior of the oven is rapidly heated by the combustion of the gases which issue from the compartments through the slits, *e*. When the oven is hot enough to effect the decomposition of the coal and the combustion of the volatile products, the compartment is charged with coal, and the upper opening is closed by putting on its cover and luting it down. Two hours later the same operation is repeated, and so on until in the course of twenty-four hours all the compartments are charged. By that time the coking in the first compartment is completed, and the coke is taken out. When empty, the compartment is charged afresh, and two hours later the second compartment is in like manner emptied and re-charged.

The Appolt ovens are expensive to build, but each yields daily 12 tons of coke, and, as there is scarcely any loss, the Duttweiler coal yields 66 to 67 per cent. of coke, whilst in a horizontal oven it would give at most 61 per cent. A defect of the Appolt system is, that the compartments in the middle of a row receive more heat than those at the ends, and with the same kind of coal yield a denser coke, a circumstance which is disturbing in metallurgical operations.

Of great importance are the coke-ovens arranged for securing the tar and ammonia. The earliest furnace of this kind was constructed by Knab, and was heated from the sole only. Carvès in 1863 added heating from the sides, and Hüssener (1883) improved the access of gas and air. In the fifty ovens erected on this plan in Gelsenkirchen, the retort is 9 metres long, conical in shape, 0·575 metre broad in the middle, and 1·8 metre high. Its available capacity is 88 per cent. of the total space, and it holds 5½ tons of dry, finely sifted coking coal, reckoning 1 cubic metre at 690 kilos. The distillation has been in uninterrupted work since November 1882. At first there were used finely sifted coals from Gelsenkirchen; they were relatively too impure, not having been washed. The sale was difficult, and the impurities produced so much waste that fat coal was chiefly used in place of gas coal. The time of preparing was at first seventy-two hours, but by a better distribution of the gases in the channels it was gradually reduced to fifty-two to fifty-six hours. In order to insure a periodical regularity in charging and emptying the retorts, these operations are effected within sixty hours. The yield was—

	Gas Coal.		Fatty Coal.
Lump coke	61·700 per cent.	...	75·00 per cent.
Small coke	3·500 „	...	0·80 „
Dirt	9·180 „	...	1·20 „
Tar	2·720 „	...	2·77 „
Ammonium sulphate . .	0·924 „	...	1·10 „

The tar is very thin; 100 kilos. yielded 58·83 distillate; 39·51 pitch distillate; 1·65 loss. A closer examination of the tar showed: Benzol, purified with sulphuric acid and soda, and several times fractionated—

Boiling between 80° and 100°	0·59 per cent.
„ „ 100° and 140°	0·49 „
Solvent naphtha	0·39 „
Phenol, purified	1·37 „
Pure anthracene	0·95 „

whilst in gas-tars the maximum yield is only 0·25 to 0·3 per cent.

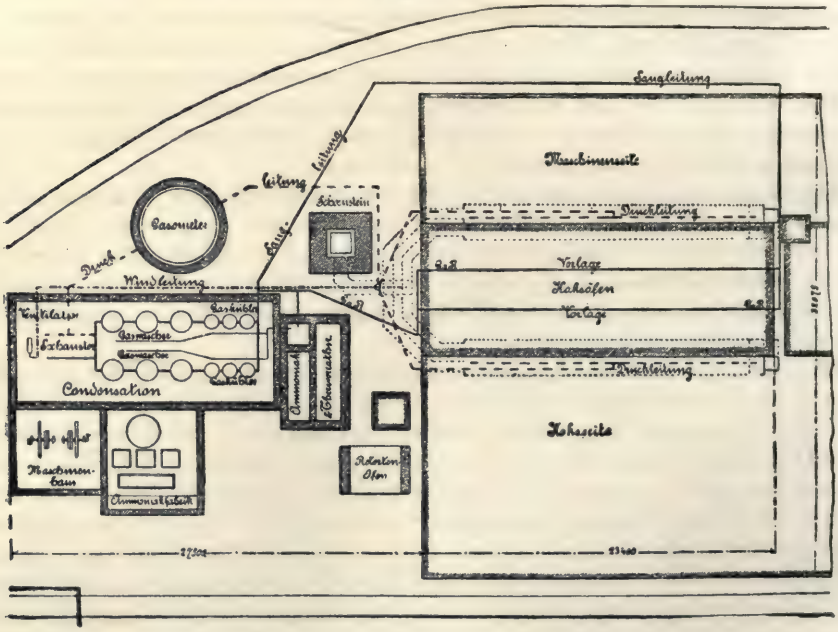
The crude gases have in the receiver above the oven a pressure = 2 mm. of water, and a temperature of 75° to 80°. The purified gases have a pressure = 90 to 110 mm. of water, and a temperature of 15°. The combustion gases contain on an average—

Carbon dioxide	8·1 per cent.
Carbon monoxide	0·4 „
Oxygen	0·3 „

and evaporate 0·91 to 1 kilo. water for each kilo. of coal put in the retorts.

G. Hoffmann (1884) combines the coke-ovens with the Siemens heat reservoirs. This arrangement was first introduced experimentally in the Silesian Coal and Coke Works at Gottesberg, without a condensation apparatus for the gas, then with very perfect apparatus for liquefaction in an installation of twenty ovens at the Pluto Mine, near

Fig. 28.

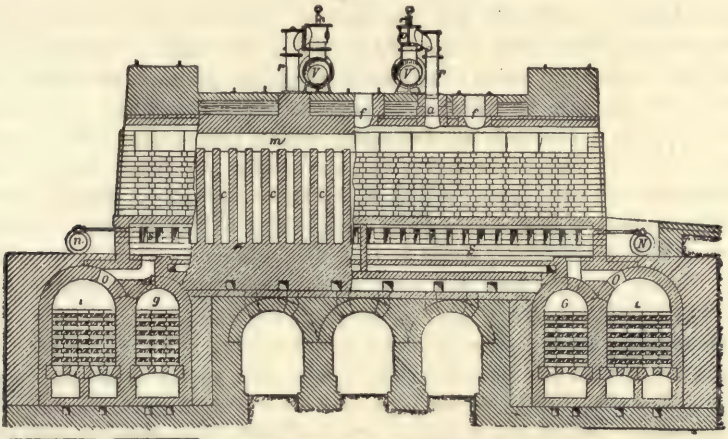


Explanation of Terms.

Maschinenhaus	Steam-engine house.	*Retortenofen*	Retort furnace.
Ammoniakfabrik	Ammonia-works.	*Druckleitung*	Pressure-duct.
——	Condensation.	*Saugleitung*	Suction-duct.
Gaskühler	Gas-coolers.	——	Gasometer.
Gaswascher	Gas-mixer.	*Schornstein*	Chimney.
——	Exhaustors.	*Maschinenseite*	Machinery shed.
——	Ventilator.	*Vorlage*	Receiver.
Windleitung	Air-duct.	*Koksofen*	Coke-oven.
Ammoniak	Ammonia-tank.	*Koksseite*	Coke-shed.
Theervorrathe	Tar-stores.		

Wanne, and in twenty ovens at the Gottesberg works. The results of these installations are so exceedingly favourable that at present 120 ovens have been built in Germany with the same arrangement for securing the by-products. Fig. 28 shows

Fig. 29.



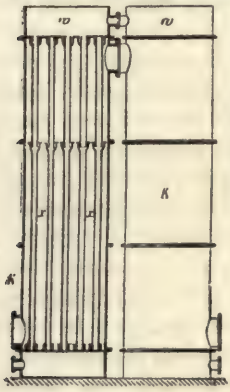


Fig. 32.

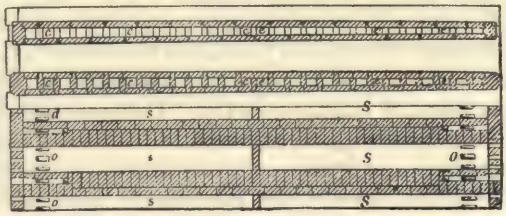


Fig. 31.

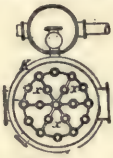


Fig. 33.

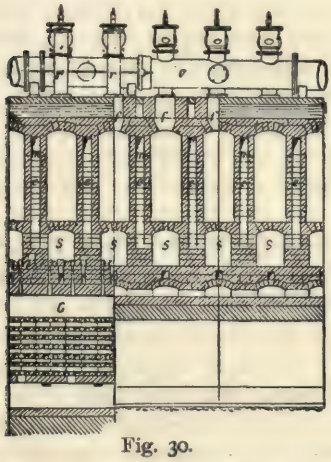


Fig. 30.

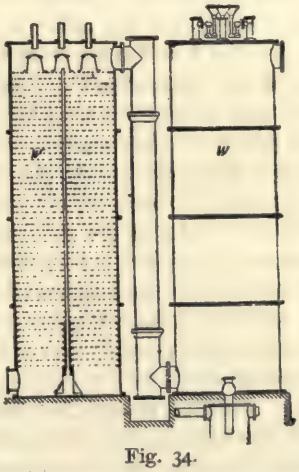


Fig. 34.

the general arrangement of the ovens and condensation at the Pluto Mine, and Figs. 29 to 34 represent the details. The coke-ovens, with vertical draughts in the sidewalls,* are 9 metres long, a clear width of 0·6 metre, a height of 1·6 metre, and

* See *Jahresber.* 1883, p. 1221.

the distance from middle to middle is 0·95 metre. In ordinary ovens without arrangements for securing tar and ammonia there are openings in the coking chambers through which the gases first pass into the lateral walls, and then into the channels in the sole, and there burn along with atmospheric air. By this the combustion chamber is heated sufficiently for the process. In the oven before us there is no direct connection between the coking chamber and the wall. Besides the openings for charging and emptying (which are closed during the process), this oven has only two apertures, *a*, in the arch by which the gases evolved may escape. In the side wall of the oven there is a channel, *m*, arranged, which passes over all the perpendicular draughts of the side wall, and renders the connection possible. Each channel in the sole is divided into two parts, *s* and *S*, in the longitudinal direction of the oven. Each part is connected with two regenerators, which lie side by side. Of these *g* and *G* serve to heat the gas to be expended in the combustion; *l* and *L* serve to heat the air required. These regenerators are long channels, set grate-like with stones so as to expose a large surface. They pass underneath the entire group, and at their end are the two air-heaters, *l* and *L*, connected, by an alternating valve, either with the pipe for introducing air or with the chimney. The gas-heaters, *g* and *G*, are likewise brought in connection either with the gas-efflux pipe, or with the chimney, by means of an especial alternating valve. When the ovens are hot, and have been charged with coal at *f*, the gases of the coals which are coking escape by the aperture *a* into the ascending pipe, *r*, and pass through the open valve, *v*, into the receiver, *V*. From hence they proceed to the condensation arrangement, where they are cooled in the refrigerators, *K*, and are washed in the scrubbers, *W* (Figs. 32 to 34). The gases are then again forced from the condensors back to the ovens (by means of the same blast, which has sucked them into the refrigerators and occasioned their entire movement), and according to the position of the alternating valve of the gas-pressure pipe, either to the regenerator *g*, or to the one, *G*, on the other side. If we assume that the gas passes to *g*, the alternating valve of the air-regenerators is placed so that the air blown in enters the regenerator *l*. This and the gas-regenerator *g* open in every oven through the adjacent apertures *o* and *d* to the channel *s* in the sole. The total current of the gases in course of combustion and of the hot products of combustion passes through the ascending channels *c* into the horizontal channel *m*, and thence descend through the vertical flues, *e*, into the channel *S* in the sole, where the spent gases escape to the chimney through the air-regenerator *L* and the gas-regenerator *G*, and give off their remaining heat to the grating of the regenerators. After about one hour, the two alternating valves are reversed, and the current then takes the opposite way. The gas passes from the condensors into the gas-regenerator *G*, and the air into the air-regenerator *L*. The combustion takes place in *S*. The current of gas, air, and of the products of combustion passes through *e* towards *m*, and then through *c* towards *s*, and through the regenerators *l* and *g* to the chimney.

Such is the original arrangement of the coke-ovens at the Pluto Mine; but the regeneration of the gas was abandoned at the very beginning, so that only the air was heated, and on the following grounds:—The proximity of the long gas- and air-regenerators may, in the possible case of leakage of their sides, lead to a mixture of air and gas in the regenerators, and consequently to fusions in them, involving irregularities in working. Further, at each reversion of the alternating valve the whole of the gas contained in the regenerators is wasted, which, on account of their large size, demands consideration. Besides, at the reversal, the escaping hot gas between the valve and the chimney meets with the hot contents of the air-regenerator, when explosions may ensue. Lastly, the volume of the air necessary for the combustion of the gas is about sixfold that of the latter. It seems, therefore, simpler and more important to raise the large volume of the air alone to a very high temperature rather than to heat, in addition, the small

volume of the gas and to withdraw the heat required for this purpose from the air. Hence the two regenerators, as they lie side by side, are used for the air only, and the gas is led out of the pipe, returning from the condensation either to *n* or *N*, according to the position of the alternating valve. In each oven a connection between the gas-pressure tube and the channel in the sole is effected by means of a small pipe fitted with a cock. The valve in the gas-pressure tube and that at the end of the air-regenerators are placed to correspond. When the gas passes through the pressure conductors into the sole channels on one side, the air sweeps through the regenerators on the same side into the same sole channels, and the combustion and the route taken by its products are those already laid down.

At present, instead of two regenerators on each side, there is only a single one in use on each side of the battery, serving merely for re-heating the air. By means of this arrangement the air for combustion can be very rapidly and intensely heated. By means of this "Siemens regeneration" the air at the Pluto Mine can be raised above 1000°, and by using for combustion air so extremely hot it is possible to employ only a part of the cold air returning from the condensation (impoverished by the loss of the tar) in order to set the coking process in action and keep the ovens sufficiently hot. It has been found in practice that there is no need to use all the gas for heating the ovens, otherwise the combustion spaces would become too hot. Hence there is much more gas than is needed for maintaining the coking process, the excess being daily 100 cubic metres per oven. The temperature is so high that the process, with a normal charge (*i.e.*, 5750 kilos. dry coal per oven), is completed in forty-eight hours; the time is often less. If the process is too rapid it is merely requisite to introduce less gas, so as slightly to reduce the temperature and bring the time to forty-eight hours. The process is quite under control, since both gas and air are forced in, and the quantities of each can be accurately regulated. The quality of the coke is excellent, and the quantity is about 7 per cent. more than in the common ovens.

The gas-refrigerators, *K* (Figs. 32 and 33), are upright iron cylinders with iron tubes, *x*, fixed in the top and the bottom. From the top piece, *w*, water flows down through the iron pipes and cools the gas, which is passing between these cooling tubes in the opposite direction. Several gas-coolers are connected together in such a manner that the cooling water which flows down from the first gas-cooler enters the second from above, whilst the gas travels in the opposite way. The gas, after its escape from the oven in the ascending tube, has a temperature of 600°–700°; in the receiver 200°–400°, according to the distance from the ascending pipe. Before the gas-coolers the heat is 75°–120°, and after them 17°–30°. By cooling, the gas parts with a large portion of tar and ammoniacal liquor, about 75 per cent. of the total liquor which the condensation furnishes. In the scrubbers, *W* (Fig. 34), there are arranged a great number of perforated metal sheets at distances of about 10 centimetres above each other. Upon the topmost, cold water is constantly dropping, so that a drizzle of water-drops is always falling from sheet to sheet so as to meet the ascending current of gas, which yields up its ammonia to the water. The ammoniacal water flows off below, and if not sufficiently strong in ammonia is pumped up again and again to meet the current of gas until it is strong enough to be saleable. Several scrubbers are placed in connection, so that the gas in passing through them comes in contact in the last with pure water only, and is enriched with ammonia in those scrubbers into which the gas first enters. The scrubbers remove the 25 per cent. of the ammonia which still remained in the gas-coolers, and at the same time eliminate very much tar. If the water employed in the scrubbers is sufficiently cold, the temperature of the gas falls to 13°. The separation of the tar and the ammoniacal liquor is effected in cisterns by means of specific gravity. The ammoniacal water is enriched in the scrubbers until it has a specific gravity of 4°–4·5° B^e, representing 1·78 per cent. of

ammonia. As the yield is about 14 per cent. of ammonia at 3°, the yield of ammonia calculated as ammonium sulphate is about 1 per cent. of the dry coal.

At the Pluto Mine the ammonia water is not converted into ammonium sulphate, but sold as liquid ammonia according to its strength. The yield of tar is on the average 3·46 per cent. for the best working month, and 2·78 per cent. for the worst month, calculated on the dry coal. These fluctuations are owing to the circumstance that sometimes the supply of water for refrigeration is insufficient. The water needed daily is 5 cubic metres per oven.

The proportion of the chief constituents of the tar (calculated as anhydrous) is, according to the researches of Knublauch—

Benzol	0·954–1·06 per cent.
Naphthaline	4·270–5·27 „
Anthracene	0·575–0·64 „
Pitch	about 50 „

A greater or less proportion of this pitch can be driven off on prolonged distillation. The residue insoluble in glacial acetic acid or in benzene is 10 to 25 per cent. of the tar.

In each oven there is a daily excess of 100 cubic metres of gas of the following composition. It has about half the candle power of that of the Cologne Gasworks. Small quantities of this gas are burnt for lighting, with very large burners. It may also serve for heating boilers, &c. It contains:—

	Coking Gas.		Cologne Gas.
Benzol vapour	0·60	...	1·54
Ethylene	1·61	...	1·19
H_2S	0·42	...	—
CO_2	1·39	...	0·87
CO	6·41	...	5·40
H	52·69	...	55·00
Methan	35·67	...	36·00
Water	1·21	...	—

This gas, as a source of heat, has the advantage that it can be conveyed to a distance. The waste heat from the regenerators, which escapes into the chimney at 420°, can be very well used for heating boilers, perhaps most advantageously with the simultaneous combustion of the superfluous gas along with hot air from the cooling channels of the coke-ovens or from the regenerators. Such a utilisation of the waste heat and of the superfluous gas for heating boilers is about to be carried out at a Westphalian coke-works.

The return from collecting the by-products depends, independently of the construction of the ovens and the condensations, and of the careful working of the process, essentially on the quality of the coal, *i.e.*, its richness in gas, tar, and ammonia. Good coking coals are especially adapted for the profitable collection of the by-products. If we assume the price of tar to be 5*s.* 6*d.* per 100 kilos., then for 10 tons of dry coal the net returns in tar for a yield of 3½ per cent. will be 19*s.* 3*d.* The yield of ammonia from the Westphalian coal is in general about 1 per cent. of the dry coal, calculated as ammonium sulphate. In Upper Silesia, the coal is richer in ammonia, and reaches 1·37 per cent. on the dry coal. If we take the market price for 100 kilos. ammonium sulphate as 27*s.* (it has since fallen to 20*s.*–22*s.*), and deducting 5*s.* for the cost of manufacture, the net returns per 10 tons dry coals (yielding 1·37 per cent. ammonium sulphate) will be 30*s.* 6*d.* We may assume that a coke-oven fitted with all appliances for securing the by-products will cost three to four times as much as a common coke-oven. Unless, therefore, the returns of such an establishment are good, the costliness of the plant stands in the way of a rapid extension of the system.

It has never been found practicable to convert the total nitrogen of coal into ammonia by dry distillation. Thus, W. Foster, on distilling a coal containing 1·73 per cent. of nitrogen, obtained 14·51 per cent. of the total nitrogen as ammonia, 1·56 as cyanogen, 35·26 in the gases, whilst 48·66 per cent. remained in the coke. Winkler* calculates that 18,000,000 tons of coal are yearly coked, from which 58,600 tons of ammonia might be obtained.

The cokes, when extracted from the ovens or retorts, are quenched with water. The three main strata of a charge of coke take up water to very different degrees. The porous top layer may absorb as much as 120 per cent. of its weight, the main mass of the charge in the middle takes up only 1½ per cent., and the bottom layer may absorb 13 per cent. As a rule, we may assume that cokes gain 6 per cent. of their weight if they are moistened with that quantity of water only which is needed to quench them. Quenched cokes thrown when cold into water do not take up one-third of the quantity which they do if thrown in when red hot.

Cokes, when properly burnt, form a uniform dense solid mass not easily broken or crushed, and having no very large bubbles or blisters. Coke prepared in kilns from baking coal has a surface like cauliflowers, and a melted appearance, not owing to fusion, but to a fine division of carbon, which is separated out at high temperatures from the hydrocarbons formed at the beginning of the process. The colour is a black-grey or iron-grey with a dull metallic lustre. The sulphur in organic combination is only driven off to a very slight extent on coking.

On account of its density and the absence of combustible gases, the combustibility of coke is so slight that it requires for ignition a strong red heat and a concentrated stream of air to maintain the fire. The combustion value ranges from 7000 to 8000 heat-units, according to the proportion of ash.

Briquettes; Block-coal.—Under this name is understood a fuel originally pulverulent, such as coal-slack, sawdust, &c., mixed with a binding ingredient, such as tar or clay, and pressed into blocks or brick-shaped masses. Here might rank pressed peat, pressed lignite, and cakes of spent tan or dye-woods.

The moulded charcoal (Paris coal) consists of charcoal made coherent by means of tar and re-charring. 100 kilos. of charcoal-dust are worked up with 33 to 40 litres of coal-tar, and the mass is moulded into the form of cylinders. These cylinders are then dried from thirty-six to forty-eight hours, and then charred in muffle furnaces. Here belongs also the pressed charcoal (pyrolite), consisting of charcoal-dust, a little soda-saltpetre, and a cohesive ingredient, such as dextrine or starch-paste. Such fuels are used in quantity in some countries for heating locomotives, for small household stoves, for drying rooms in newly built houses, where the carbonic acid given off combines with the lime of the mortar. A very imperfect fuel is the *carbonatron* introduced into commerce by Nieske, and made of charcoal-dust.

Coal blocks, &c., consist of small coal and a binding agent mixed together and pressed into shape. The binding materials are coal-tar, coal-pitch, hard and soft, natural asphalt, potato starch, treacle, &c.; also gypsum, alum, soluble glass, &c.

DEGASIFYING, GASIFYING, COMBUSTION.

The important point in the application of the fuels already mentioned (wood, peat, coal) is their behaviour when heated.

1. Heated alone: charring, coking, illuminating gas.
2. Heated with access of combined oxygen (H_2O, CO_2): water-gas.
3. With limited access of free oxygen (air): generator-gas.
4. With sufficient access of air: ordinary burning.

* *Jahresber.* 1884, p. 1249.

The processes under No. 1 are known as degasifying; those under 2 and 3 as gasification. 1 and 2 take place with absorption of heat; 3 and 4 with liberation of heat.

Degasifying.—If wood is heated, there escapes first the hygroscopic moisture; at about 170° a part of the carbon is given off as carbon dioxide, carbon monoxide, and methan; hydrogen and oxygen are split off as water, and there gradually appear the constituents of methylic alcohol, &c., acetic acid, tar, &c., whilst the residual charcoal becomes continually richer in carbon and in acetic acid. The following are the chief products from degasifying wood:—

- **Gases, 20 to 35 per cent.**
 - Carbon dioxide
 - Carbon monoxide
 - Hydrogen
 - Methan, CH_4
 - Acetylene, C_2H_2
 - Ethylene, C_2H_4
 - Propylene, C_3H_6
 - Butylene, C_4H_8
 - Benzol, C_6H_6
- **Tar, 3 to 9 per cent.**
 - Benzol, C_6H_6
 - Toluol, C_7H_8
 - Xylol, C_8H_{10}
 - Styrolene, C_8H_8
 - Naphthaline, $C_{10}H_8$
 - Retene, $C_{18}H_{18}$
 - Paraffine, $C_{20}H_{42}$ to $C_{22}H_{43}$
 - Pyrogallic dimethyl ether, $C_8H_{10}O_3$
 - Phenol, C_6H_6O
 - Cresol, C_7H_8O
 - Phlorol, $C_8H_{10}O$
 - Pyrocatechine, $C_6H_6O_2$
 - Methylesters of pyrocatechine (guaiacol and homologues)
 - $C_7H_8O_2$
 - $C_8H_{10}O_2$
 - $C_9H_{12}O_2$
 - Pyrogenous resins
- **Wood vinegar, water, &c., 35 to 45 per cent.**
 - Furfurol, $C_5H_4O_2$
 - Formic acid, CH_2O_2
 - Acetic acid, $C_2H_4O_2$
 - Propionic acid, $C_3H_6O_2$
 - Butyric acid, $C_4H_8O_2$
 - Valerianic acid, $C_5H_{10}O_2$
 - Capronic acid, $C_6H_{12}O_2$
 - Crotonic acid, $C_4H_6O_2$
 - Angelicic acid, $C_5H_8O_2$
 - Aceton, C_3H_6O
 - Methyl acetate, $C_3H_6O_2$
 - Methylic alcohol, CH_4O
 - Allylic alcohol, C_3H_4O
 - Methylamine, CH_5N
 - Hydrocœrulignon, $C_{15}H_{16}O_5$
 - Phenoles, guaiacoles, and pyrogenous resins
- **Charcoal, 20 to 30 per cent.**
 - Carbon
 - Hydrogen and oxygen
 - Ash

The gases evolved on the distillation of beechwood contain, according to the author's investigations, 58–65 per cent. carbon dioxide, 30–35 carbon monoxide, up to 5 per cent. methan and 4 per cent. hydrogen. The combustion-value of these gases is therefore trifling. The products of the distillation of peat are similar, but those of lignite have a higher value.

The products of the degasification of coal are more completely known:—

I. Coke.

II. Illuminating gas.

- Luminiferous ingredients.
 - Gases.
 - Acetylene, C_2H_2
 - Ethylene, C_2H_4
 - Propylene, C_3H_6
 - Butylene, C_4H_8
 - Allylene, C_3H_4
 - Crotonylene, C_4H_6
 - Terene, C_5H_8
 - Vapours.
 - Benzol, C_6H_6
 - Thiophene, C_4H_4S
 - Styrolene, C_8H_8
 - Naphthaline, $C_{10}H_8$
 - Methylnaphthaline, $C_{11}H_{10}$
 - Fluorene, $C_{13}H_{10}$
 - Fluoranthene, $C_{15}H_{10}$
 - Propyl, C_3H_7
 - Butyl, C_4H_9
- Diluents
 - Hydrogen
 - Methan, CH_4
 - Carbon monoxide, CO
- Impurities
 - Carbon dioxide, CO_2
 - Ammonia, NH_3
 - Cyanogen, CN
 - Cyanmethyl, C_2H_3N
 - Sulphocyanogen, CNS
 - Hydrogen sulphide, SH_2
 - Sulphuretted hydrocarbons
 - Carbon disulphide, CS_2
 - Carbon oxysulphide (?), COS
 - Nitrogen

III. Ammoniacal liquor
- Ammonium carbonate, $(NH_4)_2CO_3$
- Ammonium sulphide, $(NH_4)_2S$
- Ammonium sulphocyanide, NH_4CNS
- Ammonium chloride, NH_4Cl
- Ammonium cyanide, NH_4CN

IV. Tar, according to Schultz and others :—

		Name.	Formula.	Melting-point.	Boiling-point.
1. Neutral compounds.	A. Hydrocarbons.	1. Fatty Series.			
		Crotonylene	C_4H_6	liquid	25°
		Amylene	C_5H_{10}	,,	30
		Hexylene	C_6H_{12}	,,	71
		Hydrocarbon	C_6H_{10}	,,	85
		Jacobsen's hydrocarbon	?	,,	150
		Paraffine	?	solid	400 ?
		2. Aromatic Series.			
		Benzol	C_6H_6	+ 3°	81
		Toluol	C_7H_8	liquid	111
		Orthoxylol	C_8H_{10}	,,	141
		Metaxylol	,,	,,	141
		Paraxylol	,,	15°	137
		Styrol	C_8H_8	liquid	146
		Mesitylene	C_9H_{12}	,,	163
		Pseudocumol	,,	,,	169
		Hemellithol	,,	,,	175
		Terpene	$C_{10}H_{16}$	,,	171
		Cymol	$C_{10}H_{14}$	,,	175
		Tetramethylbenzol	,,		
		Naphthaline hydride	$C_{10}H_{10}$	liquid	205
		Naphthaline	$C_{10}H_8$	80°	217
		α-Methylnaphthaline	$C_{11}H_{10}$	—	243
		β-Methylnaphthaline	,,	32·5°	241·5
		Diphenyl	$C_{12}H_{10}$	71	254
		Berthelot's hydrocarbon	?	85	260
		Acenaphthene	$C_{12}H_{10}$	99	280
		Fluorene	$C_{13}H_{10}$	113	294
		Phenanthrene	$C_{14}H_{10}$	100	340
		Fluoranthen	$C_{15}H_{10}$	109	above 360
		Pseudophenanthrene	$C_{16}H_{12}$	115	,,
		Anthracene	$C_{14}H_{10}$	213	,,

		Name.	Formula.	Melting-point.	Boiling-point.
1. Neutral compounds.	A. Hydrocarbons.	Methylanthracene	$C_{15}H_{12}$	200	above 360
		Pyrene	$C_{16}H_{10}$	119	"
		Chrysene	$C_{18}H_{12}$	250	"
		Chrysogen	?	290	"
		Parachrysene	?	320	"
	B. Other neutral compounds.	Carbon disulphide	CS_2	liquid	47
		Ethylic alcohol	C_2H_6O	"	78
		Acetonitrile	C_2H_3N	"	82
		Water	—	0°	100
		Carbazol	$C_{12}H_9N$	238	355
		Phenylnaphthyl carbazol	$C_{16}H_{11}N$	330	above 440
		Thiophene	C_4H_4S	—	84
		Thioxene	C_6H_8S	liquid	137
2. Acids.		Hydrosulphuric acid	H_2S		
		Hydrocyanic acid	CNH		
		Carbonic acid	CO_2		
		Acetic acid	$C_2H_4O_2$	17°	119
		Phenol	C_6H_6O	42	182
		Orthocresol	C_7H_8O	31	188
		Metacresol	"	liquid	201
		Paracresol	"	36°	199
		Xylenol	$C_8H_{10}O$		
		Isodurol	$C_{10}H_{12}O_2$	215	
		α-Pyrocresol	$C_{28}H_{28}O_2$	—	195
		β-Pyrocresol	"	—	124
		γ-Pyrocresol	"	—	104
		Benzoic acid	$C_7H_6O_2$	121°	249
3. Bases.		Ammonia	NH_3	gas	
		Pyridine	C_6H_5N	liquid	115
		Pyrrol	C_4H_5N	"	126
		α-Picoline	C_6H_7N	"	134
		Lutidine	C_7H_9N	"	154
		Collidine	$C_8H_{11}N$	"	179
		Aniline	C_6H_7N	"	182
		Parvoline	$C_9H_{13}N$	"	188
		Corindine	$C_{10}H_{15}N$	"	211
		Rubidine	$C_{11}H_{17}N$	"	230
		Quinoline	C_9H_7N	"	239
		Quinaldine	$C_{14}H_9N$	"	240
		Viridine	$C_{12}H_{19}N$	"	251
		Cryptidine	$C_{11}H_{11}N$	"	257
		Acridine	$C_{12}H_9N$	107°	360+
4. Asphaltigenous compounds		Pyrogenous resins			
		Carbon			

These products are modified according to the intensity and the duration of the heat. Wright obtained from the same quantity of coal from 8·25 to 12 cubic metres of illuminating gas, according to the temperature used, and of the following composition :—

Cubic metres.	8·25.	9·7.	12.
Hydrogen	38·09 per cent.	43·77 per cent.	48·02 per cent.
Carbon monoxide	8·72 "	12·50 "	13·96 "
Methan	42·72 "	34·50 "	30·70 "
Heavy hydrocarbons	7·55 "	4·83 "	4·51 "
Nitrogen	2·92 "	3·40 "	2·81 "

Coal which, for complete degasifying, required six hours yielded gases of the following composition after the times specified :—

——	10 minutes.	90 minutes.	195 minutes.	335 minutes.
Sulphuretted hydrogen	1·30	1·42	0·49	0·11
Carbon dioxide	2·21	2·09	1·49	1·50
Hydrogen	20·10	38·33	52·68	67·12
Carbon monoxide	6·19	5·68	6·21	6·12
Methan	57·38	44·03	33·54	22·58
Heavy hydrocarbons	10·62	5·98	3·04	1·79
Nitrogen	2·20	2·47	2·55	0·78

H. Bunte* found the following composition of the purified gas during the distillation of Westphalian coal after the tenth period of fifteen minutes:—

——	x = 2.	5.	9.	13.	16.
Carbon dioxide	1·8	2·0	1·1	0·7	0·7
Heavy hydrocarbons	6·0	4·2	2·4	1·4	1·2
Carbon monoxide	8·3	7·4	6·8	6·6	6·7
Hydrogen	37·1	48·9	53·5	58·2	61·1
Methan	45·4	36·9	34·2	29·6	27·6
Nitrogen	1·4	0·6	2·0	3·5	2·7

The unpurified gas contained at the commencement 4 per cent. of carbonic acid, and towards the end 1·4.

A large part of these products is derived directly from the coal, and another portion from the original products as their mutual reaction increases with the height and the duration of the temperature. Ethylene, *e.g.*, is resolved into hydrogen and naphthaline.

According to Berthelot's researches methan forms ethylene, propylene, and perhaps the entire series of the polymeric hydrocarbons; acetylene yields benzol and a polymeric series, $(C_2H_2)_n$, &c.

Watery vapour and carbonic acid also act upon coal, as mentioned below.

There are few complete analyses of purified gas known—*i.e.*, Heidelberg gas by R. Bunsen, Königsberg gas by Blochmann, and Hannover gas by Dr. Fischer:—

——	Bunsen.	Blochmann.	Fischer.	
			I.	II.
Benzol, C_6H_6	1·33	0·66	0·69	0·59
Propylene, C_3H_6	1·21	0·72	0·37	0·64
Ethylene, C_2H_4	2·55	2·01	2·11	2·48
Methan, CH_4	34·02	35·28	37·55	38·75
Hydrogen	46·20	52·75	46·27	47·60
Carbon monoxide	8·88	4·00	11·19	7·42
Carbon dioxide	3·01	1·40	0·81	0·48
Oxygen	0·65	—	trace	0·02
Nitrogen	2·15	3·18	1·02	2·02

The combustion value of the components of coal-gas appears from the following conspectus:—

——	Mol. Weight.	Water at 0° as Product of Combustion.		Steam at 20° as Product of Combustion.	
		1 Mol.	1 Cubic Metre.	1 Mol.	1 Cubic Metre.
Benzol, C_6H_6	78	790,000	35,400	757,600	34,000
Propylene, C_3H_6	42	501,200	22,500	468,800	21,000
Ethylene, C_2H_4	28	333,400	15,000	311,800	14,000
Methan, CH_4	16	212,000	9,500	190,400	8,540
Hydrogen	2	68,400	3,070	57,600	2,580
CO	28	68,000	3,050	68,000	3,050

* *Jahresber.* 1887, p. 97.

For 1 cubic metre of coal-gas of mean composition there results the following combustion value calculated for water at 0° and steam at 20° as products of combustion :—

	Composition.	Combustion value.	
		Water. Heat-units.	Steam at 20°. Heat-units.
Benzol	0·8	283	272
Propylene	0·7	157	147
Ethylene	2·3	345	322
Methan	36·0	3,420	3,074
H	48·0	1,473	1,238
CO	8·0	244	244
		5,922	5,297

Now, 100 kilos. of good gas-coal (of about 8000 heat-units of combustion value) with careful working yields 27 to 30 cubic metres of coal-gas, or 1 kilo. of coal gives 0·3 cubic metre of gas, representing about 1600 heat-units. The gas obtained on degasifying coals represents, therefore, 20 per cent. of the total combustion value of the coal.

We have certainly as by-products from 100 kilos. of coal 50 to 70 kilos. of coke, of which from 10 to 25 kilos. are consumed in heating the retorts, also tar, ammoniacal liquor, and spent purifying mass, the value of all which is very fluctuating. If these substances can be successfully utilised, the expense of the production of gas may fall very low. This will appear from a comparison of the reports of the Cologne Gasworks for the financial years April 1, 1882–83 and 1886–87.

		1882–83.		1886–87.
Total product	cubic metres	13,447,780	...	16,963,630
„ „ sold	„	12,387,191	...	15,605,456
Loss of gas	„	1,058,489	...	1,357,374

From 100 kilos. of Westphalian coal there were obtained :—

		1882–83.		1886–87.
Gas	cubic metres	298·48	...	295·85
„ sold	„	274·94	...	272·19
Coke, saleable	kilos.	601·00	...	620·00
Tar	„	49·00	...	45·04
Ammonium sulphate	„	9·40	...	10·00
Outgoings	marks	640,516	...	985,126
„ for coal	„	430,440	...	575,551
Receipts :				
Coke	marks	255,387	...	294,340
Tar	„	119,773	...	31,988
Ammonia	„	133,693	...	91,281
Ammonium sulphate	„	19,996	...	17,293
Total	„	528,849	...	405,602

Hence 1 cubic metre cost at the works, without including interest and cost of mains, in 1882–83 only 0·83 pfennig (100 pfennige = 1*s.*); but in 1886–87 more than 3 pfennige. The cause of this is that in 1882–83 the receipts for the by-products exceeded the cost of coal by nearly 100,000 marks, but in 1886–87 fell short of the cost of coal by 170,000 marks. 100 kilos. of ammonium sulphate cost in 1882, 40·85 marks, in 1885 only 22·90 marks; 100 kilos. of tar in 1878 were worth 2·3 marks, in 1883, 5·5 marks, and in 1887, 2 marks. In 1881–82 it was even

found advantageous to burn 20,077 cubic metres of gas under the retorts, and thus to sell the main coke.*

The value of the by-products would probably fall still lower if gas was generally used as a source of heat and power. This would be very difficult, since coals suitable for the production of gas are relatively scarce.

Generator-gas.—In order to gasify the coke which remains after the degasification of the coal, oxygen must be supplied. This may be effected either with free oxygen (atmospheric air) or with combined oxygen (water or carbonic acid). The following reactions here come into play:—

1. For forming carbon monoxide: $C + O = CO = +29{,}000$ heat-units.

2. For carbon dioxide: $C + O_2 = CO_2 = +97{,}000$ heat-units.

3. For gasification with carbon dioxide: $C + CO_2 = 2CO = -97{,}000 + 58{,}000 = -39{,}000$ heat-units.

4. For decomposition with liquid water: $C + H_2O = CO + H_2 = -68{,}400 + 29{,}000 = -39{,}400$ heat-units,

but only $57{,}600 + 29{,}000 = -28{,}600$ heat-units with watery vapour at about 20°.

5. $C + 2H_2O = CO_2 + 2H_2 = -136{,}800 + 97{,}000 = -39{,}800$ heat-units if liquid water was used,

but $-115{,}200 + 97{,}000 = -28{,}200$ with watery vapour at 20°.

Of course the combustion value of the gases formed = 97,000 heat-units less heat of formation. According to the equation of decomposition, No. 4, we obtain, *e.g.*, from 12 kilos. carbon and 18 kilos. of water, 28 kilos. of carbon monoxide and 2 kilos. of hydrogen, or, jointly, $68{,}000 + 68{,}400 = 97{,}000 + 39{,}400$ heat-units.

Consequently, heat is produced only on the gasification of the carbon by *free* oxygen; if *combined* oxygen is used heat is absorbed, which must be supplied from without (on gasifying in retorts) or in the coal itself, by the introduction of free oxygen (air). The latter can take place separately or simultaneously.

In coke-generators the gasification should be arranged, as far as possible, in accordance with the first equation, since the carbonic acid formed according to the second has no more combustion value. The 28 kilos. or 22·3 cubic metres of carbon monoxide formed on the gasification of 12 kilos. carbon have consequently a combustion value of only 68,000 heat-units, instead of the 97,000 heat-units of the original coal. The 29,000 heat-units are evolved in the generator, *i.e.*, 30 per cent. of the total combustion value of the coke is likewise utilised, if the gases enter into the fire at their full heat, as is mostly the case in the coke-generators built into the retort-ovens of gasworks. But they are entirely lost if the gas is let cool down to the temperature of the air, as it would be doubtless requisite if gas were universally introduced.

Most of the gas-fires introduced industrially allow a part of this heat to be lost. A portion of the heat is even sacrificed, *e.g.*, in the Siemens gas-firing used in glass-works, iron furnaces, &c., in order to obtain a simple and regular working.

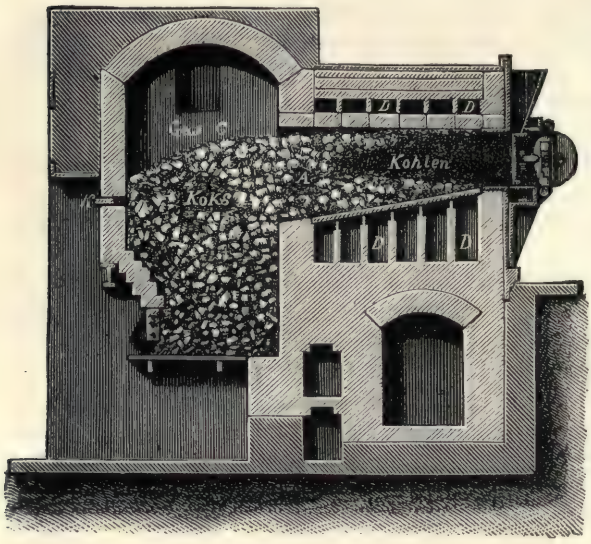
Independently of gasworks, we use in general for gas-firing, not coke, but coal. The coals are first degasified, then gasified by the introduction of atmospheric oxygen, so as to obtain a mixture of coal-gas and coke generator-gas. In Lürmann's generator these two processes are kept as separate as possible. The coal is fed uninterruptedly into the retort, *A* (Fig. 35), by mechanical power, and pushed forwards. By the channels, *D*, escape the combustion-gases, which pass away from the fire still hot, in order to furnish the heat required for the partial degasifying of the coal. The coke

* Of late years the value of tar has fallen so low that it has been sometimes profitable in England to burn the tar under the retorts instead of selling it for the manufacture of tar products.—[EDITOR.]

formed is gasified in the shaft, *b*, by the atmospheric oxygen entering; the gaseous mixture formed escapes at *C*.

In the gas-firing of Boetius, as shown in longitudinal and transverse section (Figs. 36 and 37), there lie beneath the hearth two generators, *A*. They are formed by inclined planes, *C*, oblique gratings, *D*, and side-walls, *N*, which are contracted upwards. The coal introduced at *B* gives off its gas, the coke is gasified upon the grate, *D*, so that the gases enter the flame-channel, *K*, at a high temperature. The atmospheric air introduced through the side-channels, *F*, is heated along the side-walls, *N*, of the generator, and in the horizontal channels, *H*, enters by a number of lateral apertures into the stream of gas; the flame surrounds the pots, *G*, whilst the smoke-gases escape by small chimneys, *m*.

Fig. 35.



The generator of F. Siemens is in extensive use. The coal introduced through the shaft, A (Fig. 38), slides gradually down upon the grate, *p o*, the slag formed is removed beneath, and the mixed gases escape through the pipe, *V U*.

Fig. 36.

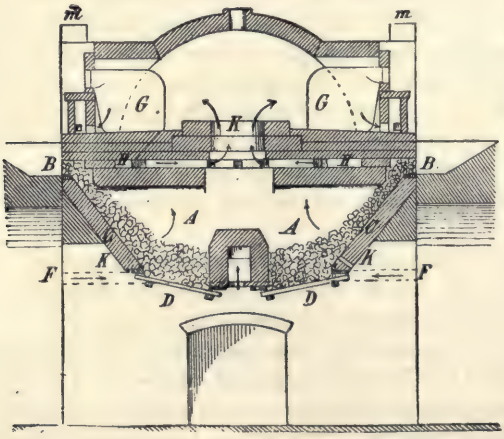
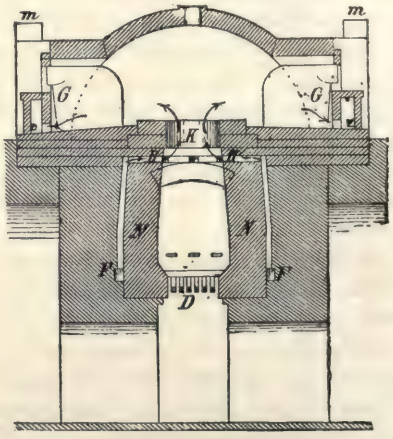


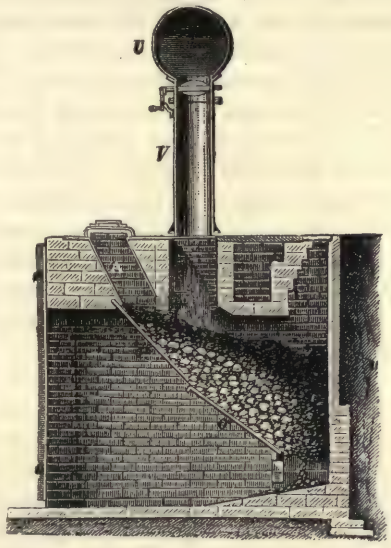
Fig. 37.



According to the kind of coal employed and the manner of working, the composition of generator-gas differs. A part of the coal-gas is decomposed, since coals before they are degasified come in contact with the instreaming oxygen, and the gas is partially burnt. Thereby the heavy hydrocarbons, and especially the hydrogen, are consumed. The water formed is then again more or less completely decomposed by the ignited coke. If the generator is worked hot, as is generally the case if no watery vapour is passed in below, decomposition sets in, whereby the proportion of the heavy hydrocarbons is like-

wise reduced. Hence it is intelligible that generator-gases contain so little heavy hydrocarbons (about 0·2 per cent.), so that it is preferable not to determine them separately, but along with the methan.

Fig. 38.



This does not complete the number of the possible transformations. Watery vapour is decomposed by carbon. According to Naumann and Pistor, charcoal is partially converted into carbon monoxide by dry carbon dioxide at 530°–560°. Dry carbon dioxide is not reduced to carbon monoxide even at 900°. The action of carbon monoxide upon water begins at about 600° with the formation of carbon dioxide and hydrogen. But if mixtures of hydrogen and carbon monoxide are heated with insufficient proportions of oxygen, then, according to the experiments of R. Bunsen, decidedly more hydrogen is burnt than carbon monoxide, so that the affinity of oxygen for hydrogen is greater than for carbon monoxide. The processes in the generator are therefore very complicated, and but partially known.

The gases from the collecting-channels of eight Siemens generators at Essen have, according to the author's experiments, the following composition :—

—	I.	II.	III.	IV.	V.	Mean.	
CO_2	6·99	5·50	5·89	3·96	4·04	5·3	
CO	22·84	26·01	22·61	24·02	23·01	23·7	30·9
Methan	2·99	2·46	1·39	1·63	0·92	1·9	
H	10·30	8·02	5·50	4·83	3·92	6·5	
N	56·88	58·01	64·61	65·56	68·11	62·6	

One kilo. of coal gave 4·52 cubic metres of generator-gas ; 1 cubic metre of this had a combustion-value of 1053 heat-units ; consequently, the 4·52 cubic metres had 4760 heat-units, whilst the coal expended had a combustion value of 7950 (steam at 20°). The gas, when cooled down to the temperature of the air, contained, therefore, only 60 per cent. of the combustion value of the coal, the rest having been expended on heating the gas.

We lose here, therefore, not merely the considerable quantities of heat which the exposed generators give off by conduction and radiation, but, further, 850 heat-units for each kilo. of coal which the long channel gives off, whilst only about 140 heat-units of the specific heat of the gas are led to the fire ; together, 4900 heat-units. This loss, if coal is not very dear, is amply compensated by the simplification and the increased certainty and uniformity of working.

The gasification of carbon by carbon dioxide occurs only as an auxiliary reaction, in order to re-convert the carbon dioxide, formed in the generator, into carbon monoxide. In gasifying carbon by watery vapour there are required almost exactly the same quantities of heat whether $CO + H_2$ or $CO_2 + 2H_2$ are produced. Of course the gaseous mixtures have almost the same combustion value if referred to liquid water.

According to equation 4 the decomposition of 18 kilos. of watery vapour at 20° requires 28,600 heat-units. This circumstance comes into play in every generator, as the atmospheric air introduced always contains watery vapour. It had been observed long ago that by letting water into the ash-pit, especially in coke generators, the grates

and the masonry of the generator are preserved, and the removal of slag is often facilitated. In consequence, water or steam is often introduced under the grate of the generator. If the generator is walled directly into the retort furnace, this introduction of heat certainly involves a loss; the higher the temperature of the escaping gases, the greater this loss. Every 18 kilos. of water decomposed in the generator carry away, according to equation 4, 39,400 heat-units, which the hydrogen formed certainly liberates on combustion. But the reconstituted water carries off as steam of 1000° about 20,000 heat-units, and if heat reservoirs (regenerators) at 500° are used, there is still a loss of about 1500 heat-units. Whether this loss is compensated by the advantages depends on local conditions; in general this will not be the case. But if the watery vapour introduced is generated by the heat of the escaping combustion-gases (which would otherwise be wasted) the loss will be smaller by 11,000 or 12,000 heat-units. It would entirely disappear only if watery vapour, produced without expense, could be introduced into the generator at the same temperature at which the combustion-gases pass away.

The introduction of watery vapour appears more favourable when the generator is at a distance from the place of its application, so that a part (greater or smaller) of the specific heat of the gas produced is given off to its surroundings. If the gas before use is cooled down to the temperature of the air, its higher combustion value seems in the first place an immediate gain, but this becomes the smaller the higher the temperature at which the products of combustion escape, and the less is the refrigeration of the generator-gas. The introduction of watery vapour into the generators cannot, hence, be universally recommended, as in most cases it is connected with loss of heat. Whether this waste is compensated by other advantages must depend on local circumstances.

Attempts have not been wanting to use generator-gases rich in hydrogen for the

Fig. 39.

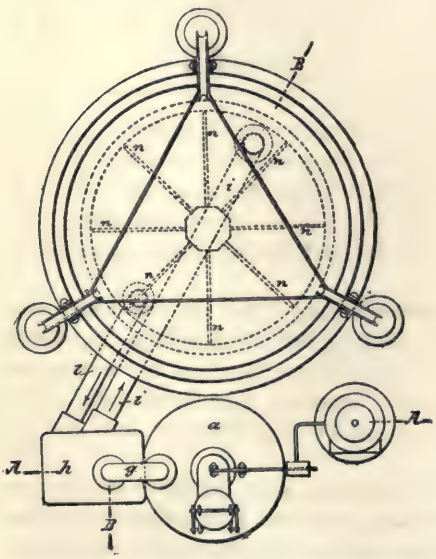
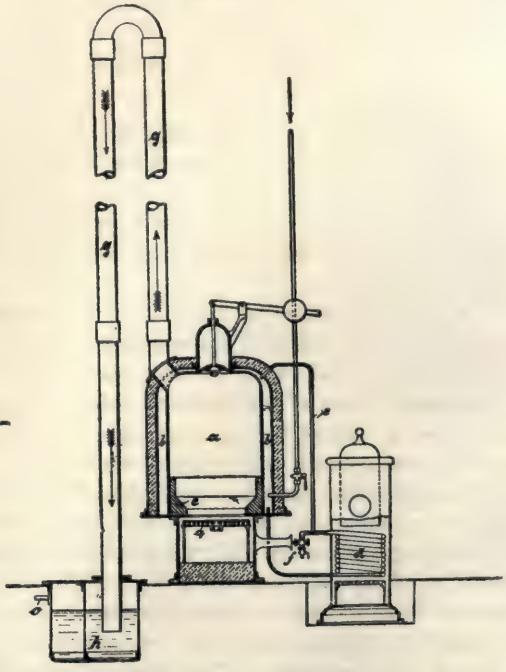


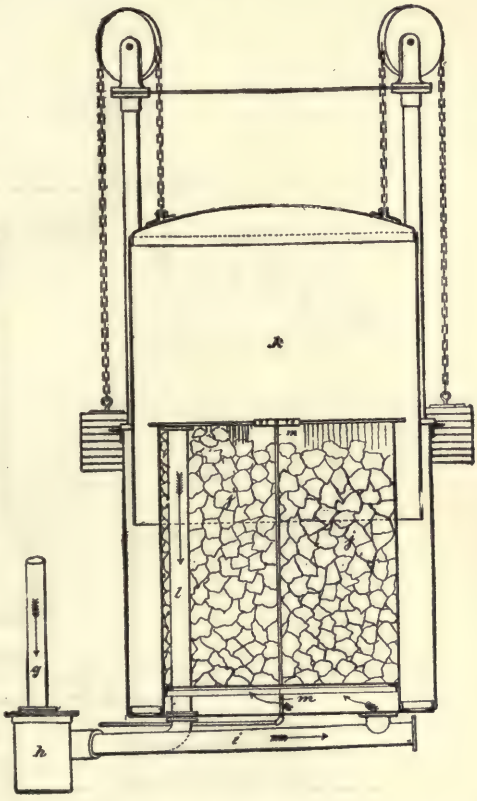
Fig. 40.



production of heat and power. This idea has been recently practically realised by Dowson. The generator, *a* (Figs. 39 and 40), has a double jacket, *b*, into which water

is driven. That part of the inner jacket exposed to the greatest heat is lined with a fire-resisting material, *c*. From the lower part of the space, *b*, the water flows to the lower part of the heating-worm, *d*, which is heated by a fire, and in which steam is constantly evolved. A part of this steam passes through the pipe *e* to the space, *b*, above the level of the water which it contains. The other part of the steam goes to the blast, *f*, through which a mixture of air and steam is blown into the fire of the gas generator. The pressure of steam in *b* compels the water under pressure to flow towards the heating-worm, *d*; the pressure in *b* can be regulated by a valve. The jacket of the space, *b*, is covered with any bad conductor of water. The heating-worm, *d*, is also fitted with a jacket, the lower part of which, enclosing the worm, is screwed to the upper part, so that the worm may be easily removed. The gas coming from the generator passes through the pipe *g* into the closed scrubber, *h*, partly filled with water, into which the pipe *g* dips, so as to be disconnected from the gas in the gas-holder, and to wash the gas coming from *a* on its way to the gas-holder. The scrubber is divided into two parts by a partition, which has an opening for the water, near the bottom. The one compartment receives the pipe *g* and a pipe *i* (Figs. 39 and 41), the latter of which leads to the bottom of the scrubber *j*. The gas passes through *i* into *j*, and ascends through the charge of coke into the gasometer, *k*. From here it passes through the pipe downwards into the second compartment of the scrubber *h*, whence it passes by another pipe to the place of its destination. The coke which fills the scrubber *j* is kept moist by water, which is conveyed by the tube *m* to the radial tubes, *n*, fitted with perforations. The water trickles through the coke, and flows through *i* to the scrubber *h*, whence it is carried out by the overflow, *o* (Fig. 40). Instead of taking the water which is to be evaporated in the worm, *d*, from the jacket, *b*, of the generator, it may be effected through the vessel placed above the worm, *d*.

Fig. 41.



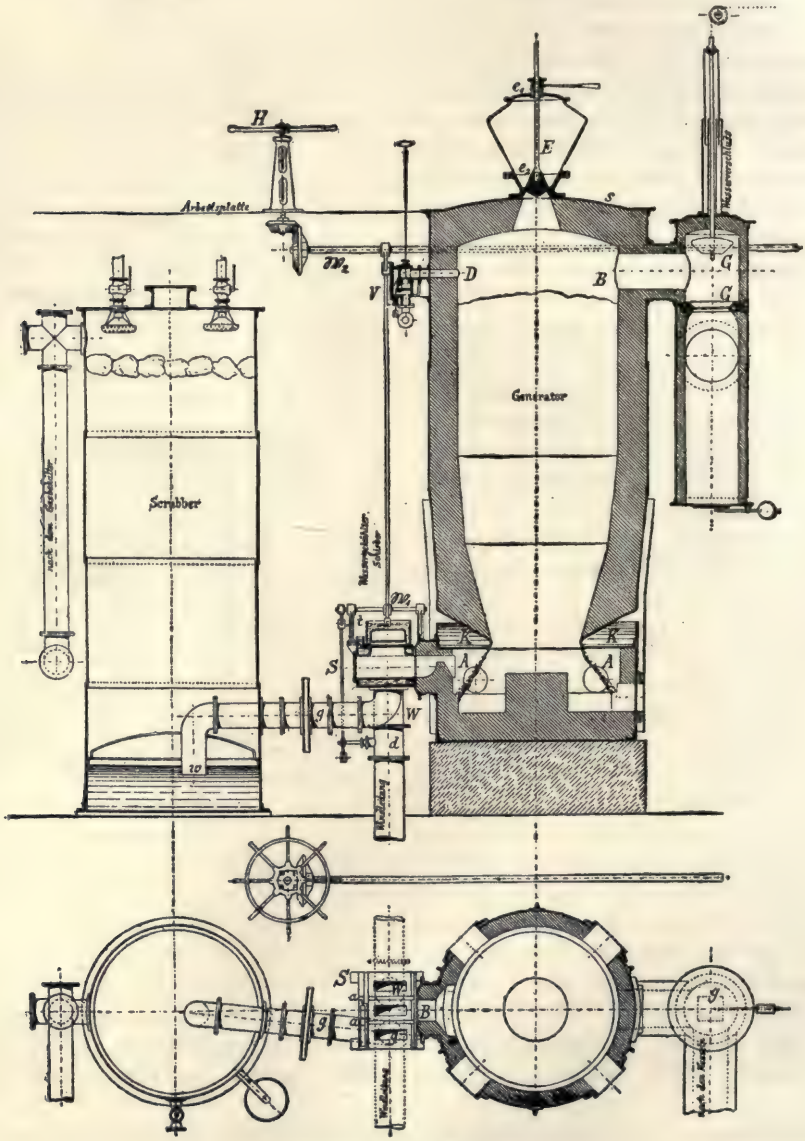
Water-gas.—That steam passed over ignited coals forms hydrogen along with carbon dioxide and monoxide has long been known. Hence the attempt has often been made to heat charcoal, coke, or anthracite in retorts, upright or horizontal, and there to introduce steam. As carbonic acid was principally formed along with hydrogen, it was sought to remove the former by means of milk of lime or caustic soda. Such a gas has been used at Narbonne for lighting, but the process has everywhere been abandoned as not economical.

In order to render the water-gas process practicable, there were used, instead of retorts heated from without, shaft furnaces into which air and watery vapour were blown alternately. Such were the arrangements of Lowe, Strong, Dwight, and others,

in use in many cities of North America. The process was adapted to European conditions by Schulz, Knaudt & Co., of Essen.

According to the arrangements at Essen and Witkowitz (*V*, Figs. 42 to 44), the

Fig. 42. Fig. 43.



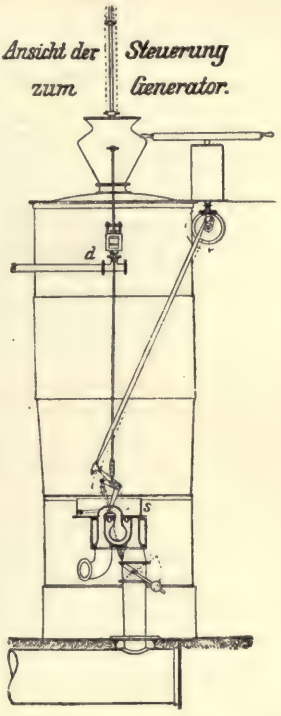
Explanation of Terms.

Arbeitsplatte	Working floor.	——	Generator.
——	Scrubber.	*Wassergekühlter Schieber*	Slide cooled by water.
Nach dem Gasbehalter	Pipe leading to the gasometer.	*Windleitung*	Air-duct.
		Wasserverschluss	Water-joint.
		Nach den Kesseln	Duct leading to boilers.

steam, which can be regulated by a sliding valve, enters at *D*, a generator filled with coke. The water-gas formed is led off below. The slide, *S*, kept cool by water, closes the air-channel as soon as the gas-channel is open, and inversely. In the same manner

the valve, *d*, fixed in the air-pipe below the point where the air enters *W* is closed as soon as the gas-pipe is open. Thus, the air is doubly shut off to prevent explosions. If the surfaces of the slide fit loosely, the small quantity of detonating gas puffs out at the openings, *a*. In Witkowitz, during the hot blast, the upper part of the slide is fixed so that the air-pipe is connected with the generator, the throttle-valve is open, and the gas-valve of the generator, *G*; the pipe through which the gas passes to the scrubber and the slide-valve, *V*, are closed. Whilst the gas is being made, *G* and *d* are closed; the upper part of the slide shuts off the airway, and establishes the connection from the generator to the scrubber; *V* is opened. The connection between the gasometer and the generator is then disturbed only by the water-joint, *w*, in the scrubber, which amounts to 100 mm. Upon the slide, *S*, there are screwed two uprights, on which is fixed an axle, $\mathfrak{W}_1$. This axle is connected with the driving axle, $\mathfrak{W}_2$. The levers upon $\mathfrak{W}_1$ move the upper part of *S*, and effect the opening and shutting of *d* and of the slide in *V*. A lever wedged upon $\mathfrak{W}_2$ effects the opening and shutting of the gas-valve of the generator; $\mathfrak{W}_2$ is turned by the hand wheel, *H*. The arrangement is such that by turning *H* to one side the upper part of *S* shuts the airway and opens the gasway. At the same time *d* and *G* are closed and the slide of *V* is opened. By turning to the other side, the upper part of *S* closes the gas-channel and opens the air-channel; at the same time *d* and *G* are opened and the slide of *V* is closed. The workman has therefore merely to turn the wheel, *H*, to correspond in order to set the apparatus either for "gas-making" or "hot-blowing," and no accident can happen from his inattention. At Witkowitz two generators are in action, each holding 10 cubic metres. Alternately steam is blown in for five minutes ("gas-making") and for ten minutes there is hot-blowing, *i.e.*, air is forced in. The generator-gas (Siemens-gas) obtained on hot-blowing is burnt under four steam boilers, and the water-gas is used for heating the Siemens-Martin furnaces.

Fig. 44.



Ansicht der Steuerung zum Generator = Connection of the scrubber with the generator.

For larger installations it is more advantageous to connect each two generators with a scrubber and a dust-collector (Figs. 44 and 46).

The generator-gas made at Essen produced 3690 cubic metres water-gas (July 21, 1887), and consumed 3256 kilos. coke. The composition of the coke was—

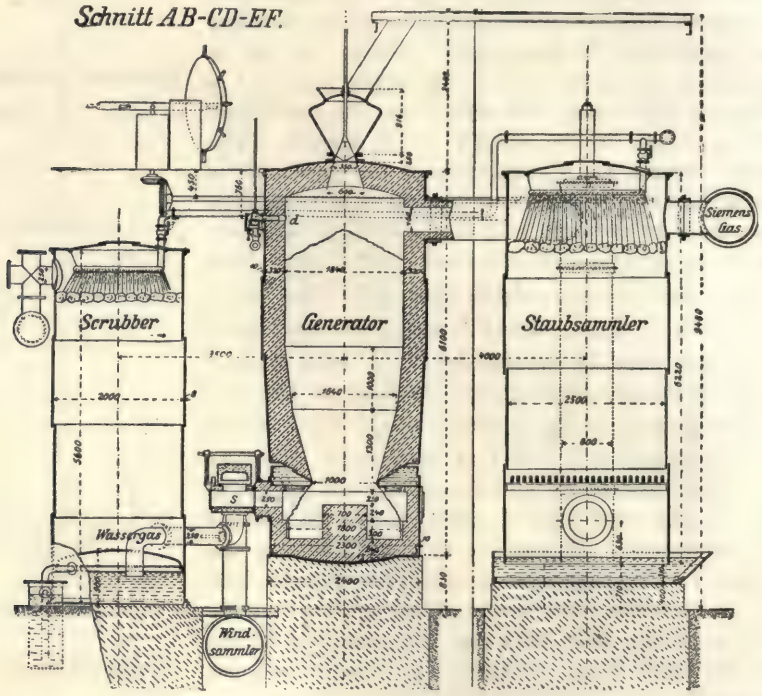
C	84·8
H	0·5
NO	2·1
Ash	10·6
Water	2·0

The generator-gases had the following mean composition :—

	In 1	6	10 Min.
CO_2	7·04	4·03	1·60
CO	23·68	28·44	32·21
Methan	0·44	0·39	0·18
H	2·95	2·20	2·11
N	65.89	64·94	63·90

Determinations of carbonic acid effected at the generator gave 1·5 to 7·2 per cent. The gases would have contained less carbonic acid if the blast had been less strong. 1 cubic metre of these gases has a mean combustion-value of 950 heat-units and contains 0·718 kilo. carbon. The temperature of the gases rose to 505°. After making

Fig. 45.



Explanation of Terms.

Section AB—CD—EF.

——	Scrubber.	——	Siemens-gas.
——	Generator.	*Wassergas*	Water-gas.
Staubsammler	Dust chamber.	*Windsammler*	Air chamber.

gas respectively for one, two and a half, and four minutes, the water-gas had the following mean composition :—

	In 1	2·5	4 Min.
CO_2	1·8 ...	3·0 ...	5·6
CO	45·2 ...	44·6 ...	40·9
Methan	1·1 ...	0·4 ...	0·2
H	44·8 ..	48·9 ..	51·4
N	7·1 ...	3·1 ...	1·9

1 kilo. of coke yielded 1·13 cubic metre of water-gas, representing 2970 heat-units, and containing $1{\cdot}13 \times 0{\cdot}477 \times 0{\cdot}5395 = 0{\cdot}291$ carbon. The remaining 0·557 kilo. of carbon yielded 3·13 cubic metres of generator-gas. Of the 7000 heat-units of the coke there are found in the

Water-gas . . .	2970 heat-units	= 42 per cent.
Generator-gas . . .	2970 „	= 42 „

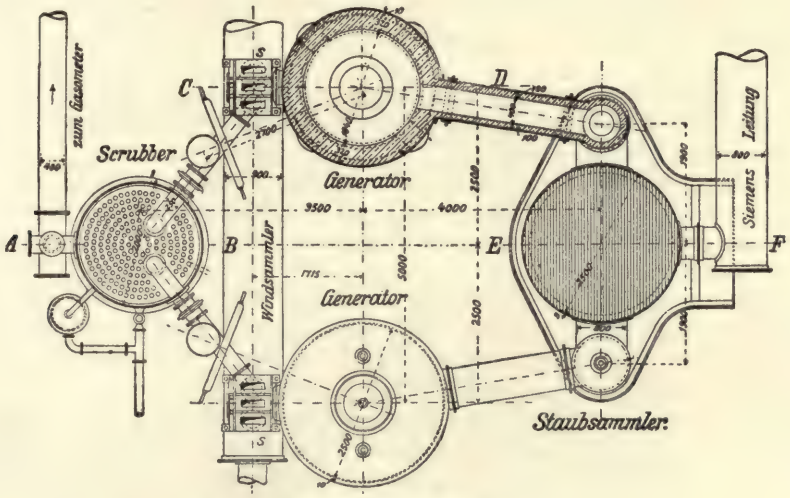
At Essen, to a small extent at Sulzer, and in some other places water-gas is used to give light by means of Fahnehjelm's magnesium burner. Taking the cost of the

mains into account, the price of water-gas would in many places be higher than that of coal-gas, but in others lower—lower even than petroleum.

Water-gas may find extensive application in metallurgical operations, in chemical works, and in the laboratory, especially as it has the advantage of not depositing soot on the apparatus to be heated, and of giving out a higher temperature.

Fig. 46.

Grundriß.



Explanation of Terms.

GROUND PLAN.

Zum Gasometer	Pipe leading to—Gasometer.	*Staubsammler*	Dust chamber.
„ *Scrubber*	Scrubber.	*Siemens Leitung*	Siemens-conduction.
„ *Generator*	Generator.	*Windsammler*	Air-collector.

The use of water-gas will become more general as soon as it is produced from coal instead of coke, since it appears irrational first to coke the coal in a separate apparatus. A remunerative production of ammonia is, however, scarcely practicable in the direct production of generator-gas and water-gas from coal, and that of tar (even at improved prices) seems out of the question.

Whilst 1 kilo. of the best coal gives at the most 0·3 cubic metre of illuminating gas, we obtain from 1 kilo. of common coke 1·13 cubic metre of water-gas and 3·13 cubic metres of generator-gas, which together contain 84 per cent. of the combustion value of the coke used. If the coal is partially degasified, then at once gasified, and the luminous gas mixed with the water-gas, we have a gas containing—

Heavy hydrocarbons	1 per cent.
Methan	8 „
Hydrogen	48 „
Carbon monoxide	37 „
Carbon dioxide	3 „
Nitrogen	3 „

and having a combustion value of about 3250 heat-units per cubic metre. Along with this richer gas we have as by-products tar, ammonia, and cyanogen, as in common coal-gas, and the corresponding proportion of generator-gas, as in the ordinary water-gas process.*

* The great objection to water-gas has been its dangerous character. As will be seen from the above analysis, it contains from 30 to upwards of 40 per cent. of the fearfully poisonous con-

HEATING ARRANGEMENTS.

If wood, peat, lignite, or coal is heated, it is degasified in the manner already described. If atmospheric oxygen is present, and if the temperature is sufficiently high, the gases take fire and burn with a luminous flame. The residual charcoal or coke does not burn with a flame, but glows, the combustion taking place only on the surface. If the air, after its oxygen has been completely converted into carbonic acid, remains in contact with the fuel, and if the temperature is sufficient, the carbonic acid (carbon dioxide) takes up another atom of carbon, $CO_2 + C = 2CO$, and forms carbonic oxide (carbon monoxide).

In our ordinary fires, domestic or industrial, these processes take place simultaneously. To effect complete combustion there is required a sufficient supply of oxygen (or air) and a sufficient temperature.

If oxygen is deficient, the combustion is imperfect; from the charcoal or coke there is formed carbon monoxide (a colourless gas); the gas produced on the degasifying of wood or coal gives a smoky flame, as the hydrogen combines with the oxygen by preference, so that the heavy hydrocarbons and the other constituents of tar liberate more or less free carbon. If undecomposed particles of tar escape along with the soot, it becomes adhesive, attaches itself to solids, and has a very unpleasant smell. If a fire is to be smokeless, the complete combustion of the gases and the accompanying tarry vapours must be effected; degasified fuel burns without smoke.

For the complete combustion of the volatile matter, especially the tar, a sufficient temperature is necessary. As this is lowered by the immediate withdrawal of heat by cold surfaces, water, and superfluous air, the mixture of gases or vapours to be burnt must not before complete combustion come in contact with cold surfaces (stoves should be lined with fire-clay or stone, not with iron), and the fuel must be employed as dry as possible (coal should not be moistened). It follows that the numberless proposals for the *combustion* of smoke are useless. The *formation* of smoke can be prevented, but smoke, when once formed, is so hard to burn that the task may be pronounced practically impossible.

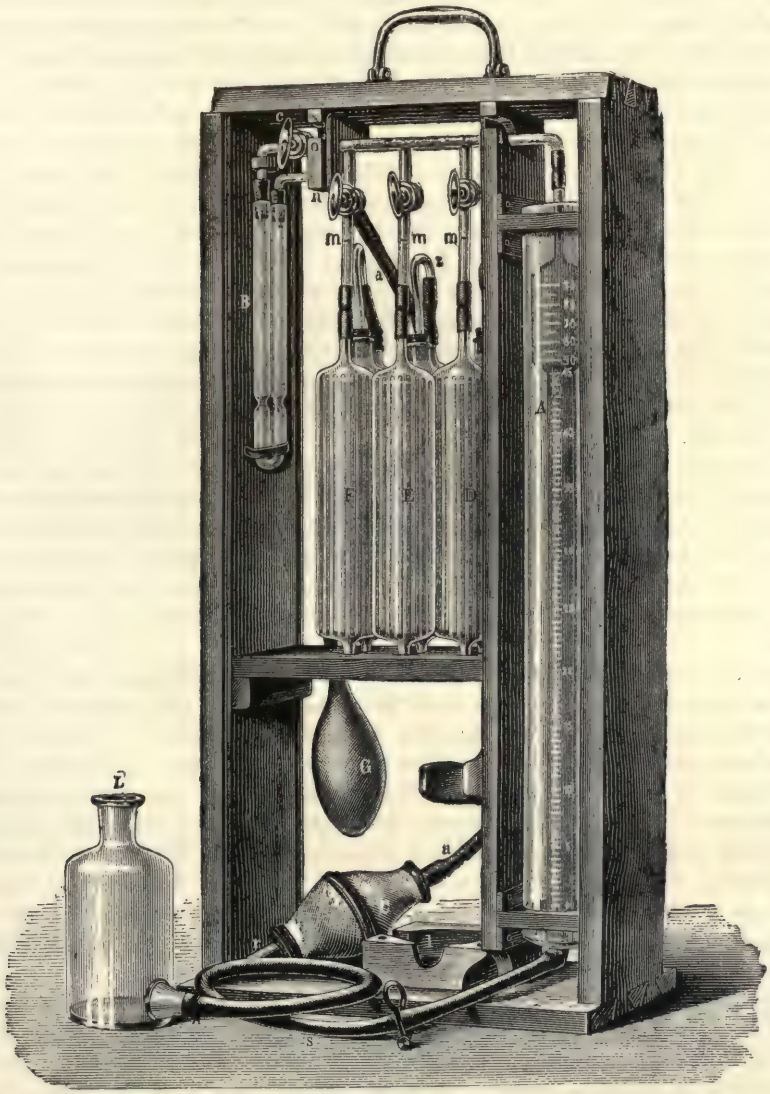
Gas Analysis.—A correct estimate of a firing can be effected only on the basis of gas analysis. With the following apparatus, made by W. Apel, mechanician to the University of Göttingen, the author has executed thousands of gas analyses.

The lower part—holding 45 c.c.—of the burette, A (Fig. 47), used for measuring the gas under examination, which is enclosed in a wide cylinder filled with water in order to obviate fluctuations of temperature, is divided into tenths of a c.c., but the upper part is graduated only into entire c.c. The thick glass capillary tube with the glass cocks is fastened at both ends at i in a section of the partition, and at o in a

stituent, carbon monoxide, which, in good coal-gas, does not exceed 8 per cent. Hence a very slight escape is sufficient to prove fatal. Two men at Leeds lost their lives from accidentally inhaling air thus contaminated, and even the medical men commissioned to make an autopsy of the bodies were rendered seriously ill. The danger is the greater as water-gas is, *per se*, inodorous, so that a leakage is not detected as rapidly as is the case with ordinary coal-gas. For this evil a remedy has been devised by Mr. W. Crookes, F.R.S., and Mr. F. I. Ricarde-Seaver, F.R.S.E. The process, which is simple and inexpensive, is fully described in their patent, No. 10,164 of 1889. They cause the water-gas, as at present produced, to pass at red heat over a mixture of caustic soda and quicklime. The water in the soda is decomposed, its oxygen going to the carbon monoxide and converting it into carbonic acid, which latter instantly unites with the soda and lime, while the hydrogen is liberated and takes the place of the carbon monoxide in the water-gas. The mixture, when spent, can be revivified by dissolving out the carbonate of soda with water and causticising it afresh in the ordinary manner. The poisonous character of the gas is thus entirely removed without injury to its combustion value, and it can be easily enriched if required for illuminating purposes.—[EDITOR.]

small support in the cover of the box. The four glass cocks close perfectly, and never stick fast if handled in an intelligent manner. The cock tube is bent round at its front and connected with the U-tube, B, the limbs of which contain cotton-wool, whilst there is a little water in the lower bend, in order to keep back any soot or dust, and to saturate the aspirated gas with water before it is measured. The end of the three-way cock which is turned backwards is connected by a caoutchouc tube with the caoutchouc

Fig. 47.



sucker, C, by means of which it is easy to fill the gas entrance tube and B with the gases to be examined. The combination of the gases takes place in the U-shaped vessels, D, E, and F, fixed below in notches and connected by short caoutchouc tubes with the cock tube, and filled with glass tubes to increase the surfaces of contact. As the mark m is above this point of connection, it is always moistened with the liquid concerned, and is thus easily kept perfectly tight. The other end of the U-tube is closed with a

caoutchouc stopper containing a small glass tube, x; the small tubes are connected in common with a slack caoutchouc ball, holding about 200 c.c. to keep off oxygen.

When the apparatus is to be used, the cylinder inclosing the burette, A, and the flask, L, are first filled with distilled water. To fill the three absorption bottles, the stoppers with the glass tubes, x, and the caoutchouc ball, G, are taken off, and there is poured into D about 110 c.c. potassa-lye of sp. gr. 1·20 to 1·28, so that it is about half full.

Further, we dissolve 18 grammes pyrogallol in 40 c.c. hot water, 70 c.c. of potassa-lye of the above strength are added, and the mixture is poured into E, to take up oxygen. For determining carbon monoxide, we place beforehand 35 grammes copper chloride with 200 c.c. of strong hydrochloric acid and a few clippings of sheet-copper in a well-stoppered bottle, and let them stand for two days with frequent shaking; 120 c.c. of water are added, and the vessel F is charged from this solution. The three glass cocks are closed, the cock c is set vertically, and the bottle L is lifted up so that the water fills the burette, A, the cock c is turned a quarter to the left so that the second aperture leads to the tube B, the cock of D is opened, the bottle L is lowered, and the pinch-cock fixed upon the tube s is cautiously opened so that the potassa-lye rises to the mark m when the cock is closed. In like manner the liquids of the two other vessels are drawn up to the mark m, keeping the eye constantly fixed upon the *ascending* liquid. The three stoppers with the glass tubes, x, are then inserted air-tight. Into the tube B there is first poured a little water, both limbs are loosely filled with cotton-wool, the stoppers are re-inserted, and the little tube, n, is connected by a caoutchouc tube with the glass tube, or at high temperatures with the porcelain tube, which is luted with clay air-tight into the chimney, &c., in order to prevent the access of atmospheric air.

To ascertain if the apparatus is air-tight, the cock *c* is placed vertically, the caoutchouc pipe is pressed closely to the tube in the chimney either with the pinch-cock or with the hand, and the pinch-cock of s is opened. The water-column in A sinks a little, but it must then remain standing immovably. A continued slow sinking must be remedied either by fitting the caoutchouc pipe more closely, or pressing in the stoppers, or lubricating the glass taps with vaselin mixed with a little paraffine.

After the burette, A, has been filled with water up to the mark 100, by lifting the bottle L, the cock c is placed so that the connection of the aspirator, C, with the chimney is established through the tube B, suction is effected by pressing C ten to fifteen times, until the entire channel is filled with the gases in question. This is best effected by pressing C with the left hand, closing the tube *r* with the thumb of the right hand, letting the ball expand by opening the left hand, raising the thumb, compressing C again, and so on until the object is effected. The cock c is then again set vertically, the pinch-cock of *s* is opened, and the bottle L is lowered, so that the burette, A, is filled to 0° with the gases to be examined; thereupon c is again closed by turning it a quarter to the left. The gas is now shut in between the four glass cocks and the column of water in A.

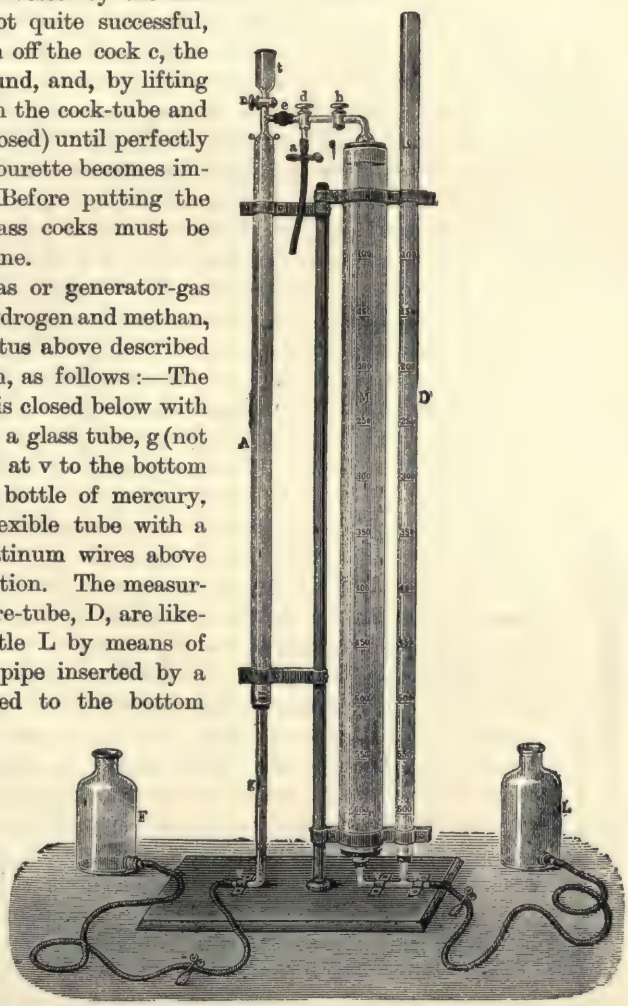
For determining the carbon dioxide, the cock of D is opened, and L is raised with the left hand, so that on opening the pinch-cock at s with the right hand the gas passes over into D, L is lowered again until the potassa-lye in D reaches to the junction of the flexible tube under m, and the gas is once more driven into the potassa vessel by raising L. On lowering L and cautiously opening the pinch-cock, the potassa-lye is again allowed to rise to the mark m, the glass cock is closed, the pinch-cock is opened, the bottle L is held close to the burette so that the water in both vessels stands at an equal height, the pinch-cock is again closed, and the residual volume is read off. The level of the water shows directly the percentage of the carbonic acid by volume in the gas. In the same manner the gas is passed two or three times into E, until no

further decrease of volume ensues; the reading gives the joint volume of carbon dioxide and oxygen, whilst carbon monoxide is further absorbed by a similar treatment in F. In ordinary fires it is generally needless to examine for carbon monoxide if a few per cents. of oxygen have been found.

When the analysis is thus completed the cock c is again placed horizontally, L is lifted, the pinch-cock is opened, and the water is let flow up to 100 in the burette, c is again set vertically, the channel is again filled with the gas by means of C, and a fresh determination is made. If, as is usual, no carbon monoxide is present, with a little experience it will be found practicable to effect every five minutes an analysis accurate to one-tenth per cent.

If after 100 to 200 analyses the absorption becomes sluggish, the vessels are emptied by means of a siphon, rinsed with distilled water, and filled anew as before. If by inattention the absorption liquid should rise in the cock-tube, the bottle L is raised, the pinch-cock opened, and the solution is thus rinsed back into the vessel by the distilled water. If this is not quite successful, the flexible pipe, a, is taken off the cock c, the latter is turned half way round, and, by lifting L, water is let flow through the cock-tube and the cock c (the others are closed) until perfectly clean. If the water in the burette becomes impure, it must be changed. Before putting the apparatus away all the glass cocks must be lubricated afresh with vaseline.

Fig. 48.



If in examining water-gas or generator-gas we wish also to determine hydrogen and methan, we may connect the apparatus above described without a mercurial trough, as follows:—The working-tube, A (Fig. 48), is closed below with a caoutchouc stopper having a glass tube, g (not too narrow), which is fixed at v to the bottom plate, and connected with a bottle of mercury, F, by means of a strong flexible tube with a screw pinch-cock. The platinum wires above are fused in for electric ignition. The measuring-tube, M, and the pressure-tube, D, are likewise connected with the bottle L by means of a glass tube and a flexible pipe inserted by a caoutchouc plug and secured to the bottom plate. It is advisable to fix a small brass cap round the point of connection, e, since it may otherwise happen that, on exploding the gaseous mixture by means of an induction spark, the caoutchouc connection may spring off.

In executing the analysis, the tubes A, M, D (the latter up to O), are filled with mercury by raising the two bottles, the pinch-cocks on the flexible pipes and the three glass cocks are closed, so that the end of the pipe a

remains filled with water (or mercury), one of the drawn-out ends of the glass globe containing the sample of gas is introduced, the point is broken off within the flexible pipe, the other end is plunged into water and its point also is broken off, the cock d is turned so as to make connection with the tube A, and the sample of gas is sucked over to A by lowering the mercury bottle, F. The cocks d and h are now turned round 90°, and the needful quantity of gas is forced into the measuring-tube, M, by raising the mercury bottle, F, and lowering the other bottle, L. If there is contained in the tube A a residue of gas and any water which has been drawn over, they are forced outwards by the cock d. The sample of gas is measured, 0·6 to 0·8 c.c. of potassa-lye are introduced into the tube A through the funnel, t, the sample of gas is passed over from M and A, and, after the carbon dioxide has been absorbed, again to M. The potassa-lye is only allowed to rise to a mark immediately before d, which can be seen during the calibration of the tube. When the carbonic acid has been determined and the presence of oxygen tested with pyrogallol, the tube A must be carefully cleansed up to the cock d, as otherwise after the explosion a part of the carbonic acid formed is immediately dissolved and the contraction is thus rendered great. This is effected by pouring about 5 c.c. water into the funnel, t, lowering the bottle F, and then lifting it so that the liquid flows off through the flexible pipe, a, into a bottle connected by means of a short glass tube and a long flexible pipe. This is repeated three or four times. If by inadvertence any potassa-lye has passed beyond d up to h, or even to M, after the cleansing of the tube A has been completed water is again let enter through the funnel, t; F is raised until all air has been removed through the cock n and the flexible pipe a, when the pinch-cock is closed on a and the water is allowed to pass towards M by turning the cocks d and h round for 90°. Then the bottle L is raised and F is lowered, so that the sample of gas, the water, and some mercury pass over to A. When this is done the specimen of gas is let return to M, the cock d is closed towards M as soon as the liquid almost touches it, then immediately also h, and the water is again let flow off through a. Care is taken that the end of the flexible pipe a always remains filled with water or mercury. A few drops of liquid should also remain in the funnel, t. The absorption of carbon dioxide and oxygen is much promoted by letting the sample of gas pass ten or twelve times from one tube to the other without the liquid touching the cock-tube. For this purpose the bottles, F and L, are taken one in each hand and lowered alternately, keeping the eye constantly upon the liquid as it ascends in A and M.

Fig. 49.



The oxygen required for burning the combustible gases is best obtained electrolytically. This can be conveniently effected by means of A. W. Hofmann's apparatus for the decomposition of water, or with the U-tube (Fig. 49) fixed upon a simple foot and filled up to the cock with water containing sulphuric acid. The point of the tube *s* (its platinum electrode is connected with the positive pole of a Taucher battery) is placed in the end, a, of the flexible tube, filled with water, and the oxygen is let pass over to A and thence into the tube M. If the end of the tube a is completely filled with mercury, the oxygen may be at once passed into M. After measurement, the gaseous mixture is driven to A, the spark is passed, the contraction determined as usual, the carbon dioxide and the nitrogen are determined and calculated as given below. If the gaseous mixture is not so far known that the effect of the explosion may be judged with certainty in the first place, about 100 vols. are allowed to pass to A, the cocks d and h are closed, the mercury-bottle F is set on the bottom plate of the apparatus, the pinch-cock is opened so that the gas is strongly expanded, and the spark is let pass over. It is then easily seen whether, on exploding the larger residue, a diminution of pressure must be applied to reduce the force of the explosion. If the gas contains less than 30 per cent. of combustible ingredients, it may be placed under

an increased pressure ; if up to 30–40 per cent., it should be exploded at the ordinary atmospheric pressure ; up to 40–50 per cent., at a reduced pressure.

In manufacturing laboratories water may often be used in the bottle L, but in F mercury is necessary. The tube D may be dispensed with ; M is graduated, not in millimetres, but in 100 vols. ; the water level in the bottle L and the tube M is placed at an equal height before reading off, so that—as during the short time required for an analysis the temperature and the height of the barometer may be regarded as constant—all calculations are needless. But as this latter advantage can only be secured by placing the mercury in M and D exactly at the same height before each reading, the author prefers the apparatus (Fig. 48) with mercury in both bottles.

As a lubricator for the cocks, the author recommends a mixture of melted caoutchouc and vaseline. This is prepared by melting two parts of pure caoutchouc at the lowest possible temperature in a covered porcelain crucible, adding one part of vaseline, and stirring till cold. The readings are calculated for 0° and 1000 mm. pressure of mercury according to—

$$V = \frac{v\,(B - b - e)}{1000\,(1 + (0{\cdot}00366 \times t))}$$

with the aid of the tables.

Tension of the Vapour of Water according to Regnault :—

t = temperature Centigrade ; m = tension in millimetres.

t.	*m.*	*t.*	*m.*	*t.*	*m.*	*t.*	*m.*
12·0	10·46	15·0	12·70	18·0	15·36	21·0	18·50
12·2	10·60	15·2	12·86	18·2	15·55	21·2	18·72
12·4	10·73	15·4	13·03	18·4	15·75	21·4	18·95
12·6	10·88	15·6	13·20	18·6	15·95	21·6	19·19
12·8	11·02	15·8	13·37	18·8	16·15	21·8	19·42
13·0	11·16	16·0	13·54	19·0	16·35	22·0	19·66
13·2	11·31	16·2	13·71	19·2	16·55	22·2	19·90
13·4	11·46	16·4	13·89	19·4	16·76	22·4	20·14
13·6	11·61	16·6	14·06	19·6	16·97	22·6	20·39
13·8	11·76	16·8	14·24	19·8	17·18	22·8	20·64
14·0	11·91	17·0	14·42	20·0	17·39	23·0	20·89
14·2	12·06	17·2	14·61	20·2	17·61	23·2	21·14
14·4	12·22	17·4	14·79	20·4	17·83	23·4	21·40
14·6	12·38	17·6	14·98	20·6	18·05	23·6	21·66
14·8	12·54	17·8	15·17	20·8	18·27	23·8	21·92

Log. 1 + 0·00366 . *t.*

t.	log.	t.	log.	t.	log.	t.	log.
12·0	0·01867	15·0	0·02321	18·0	0·02771	21·0	0·03216
12·2	0·01897	15·2	0·02351	18·2	0·02801	21·2	0·03246
12·4	0·01928	15·4	0·02381	18·4	0·02831	21·4	0·03275
12·6	0·01958	15·6	0·02411	18·6	0·02861	21·6	0·03305
12·8	0·01989	15·8	0·02441	18·8	0·02891	21·8	0·03334
13·0	0·02019	16·0	0·02471	19·0	0·02921	22·0	0·03363
13·2	0·02049	16·2	0·02501	19·2	0·02951	22·2	0·03393
13·4	0·02079	16·4	0·02531	19·4	0·02980	22·4	0·03422
13·6	0·02110	16·6	0·02561	19·6	0·03009	22·6	0·03452
13·8	0·02140	16·8	0·02591	19·8	0·03039	22·8	0·03481
14·0	0·02170	17·0	0·02621	20·0	0·03068	23·0	0·03510
14·2	0·02200	17·2	0·02651	20·2	0·03098	23·2	0·03539
14·4	0·02230	17·4	0·02681	20·4	0·03128	23·4	0·03568
14·6	0·02261	17·6	0·02711	20·6	0·03157	23·6	0·03598
14·8	0·02291	17·8	0·02741	20·8	0·03187	23·8	0·03627

Reduction of the Readings of the Barometer to 0°.

B – *b*.	Correct.	B – *b*.	Correct.	B – *b*.	Correct.
400	0·0684	600	0·1027	800	0·1369
420	0·0719	620	0·1061	820	0·1403
440	0·0753	640	0·1095	840	0·1437
460	0·0787	660	0·1129	860	0·1471
480	0·0821	680	0·1163	880	0·1506
500	0·0856	700	0·1198	900	0·1540
520	0·0890	720	0·1232	920	0·1574
540	0·0924	740	0·1266	940	0·1608
560	0·0958	760	0·1300	960	0·1643
580	0·0992	780	0·1335	980	0·1677

E.g., in an analysis the reading of the barometer was 756·6 mm. at 20·8°, so that, with a correction of 2·7 mm. for the glass scale, B, = 753·9 mm. To the reading of the measuring-tube, M, = 546·0, corresponds v, = 553·5. The position of the mercury in the pressure tube, D, was also 546·0, consequently $b = 0$, and as, at 20·8°, $e = 18{\cdot}3$ mm., $(B - b - e) = 735{\cdot}6$ mm. and V = 378·34, as—

Log. 553·5	2·74312
Log. 735·6	2·86664
Log. 1000 (1 + 0·00366 × 20·8)	3·03187
Therefore log. V	2·57789
and V	378·34

Collocated with the second reading :—

M.		v.		D.		(B – b – e.)		V.
546·0	...	553·5	...	546·0	...	735·6	...	378·34
370·0	...	378·8	...	29·1	...	1075·3	...	378·41
								Mean 378·38

If the two readings do not agree to at least 0·4, there is an error, and the experiment must be repeated.

Fig. 50.



In order to preserve samples of gas for a length of time, the gas is drawn by means of the small caoutchouc aspirator, C (Fig. 47), through a glass globe holding 100 c.c. (Fig. 50), and sealed off before the lamp at c, c. In order to perform this sealing even in the open air, the author uses a small oil lamp, n, with a brass screen, shown in section (Fig. 51). The nozzle of the blow-pipe, e, is admitted

Fig. 51.

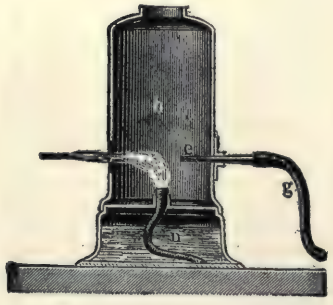
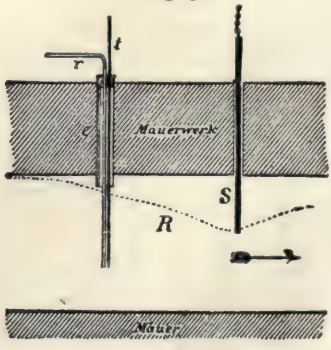


Fig. 52.



Mauerwerk Masonry.
Mauer Wall.

through a corresponding aperture, opposite to which is another opening through which the blow-pipe flame issues.

The sample of gas must be drawn through a glass or porcelain tube (not iron), and taken at a point where the gases are already mixed. In ordinary fires this takes place where the gases of combustion leave the apparatus (steam boiler, &c.), and in any case before the draught-slide, *S* (Fig. 52), as cold air is drawn in by the split in the masonry. It is convenient to have fixed in the vault of the smoke-channel a tube, *e*, 2 or 3 c.m. in width, a piece of a gas-pipe, luting it well, and inserting in it, by means of a caoutchouc plug, the thermometer, *t*, and the glass tube, *r*, for taking specimens. The mercurial vessel of the thermometer (1 metre in length) and the lower aperture of the glass tube, *r*, should be in the middle of the current of gas, as the figure shows.

The loss of heat in the smoke-gases appears from the following calculations. If the gas-analyses made during an experiment show on the average *k* per cent. carbon dioxide, *o* per cent. oxygen, and *n* per cent. nitrogen, the proportion of air consumed to that theoretically required is, when the air contains *x* per cent. of oxygen and *z* per cent. of nitrogen—

$$v = \frac{x}{x - (z\,o : n)} \text{ or } \frac{n}{n - (z\,o : x)} \text{ or } \frac{21}{21 - (79\,o : n)}$$

for 21 per cent. oxygen; 1 kilo. of the coal with *c* per cent. of carbon gives = 1·854 *c* : 100 = K cubic metre carbon dioxide (at 0° and 760 mm.), K *o* : *k* = O cubic metre O and K *n* : *k* = N cubic metres of nitrogen. The quantity, W, of the watery vapour contained in the smoke-gases is calculated from the moisture of the coal (0·01 *w*), that formed by the combustion of the hydrogen (0·09 *h*), and that contained in the air serving for combustion (*v* L *f*). The total quantity of the combustion-gases from 1 kilo. of coal is therefore—

$$\mathrm{K} + \frac{\mathrm{K}\,(o + n)}{k} + \frac{2s}{286{\cdot}4} + \frac{\mathrm{W}}{0{\cdot}805} \text{ cubic metre at 0° and 760 mm.}$$

$$\text{or } \frac{2{\cdot}667\,c}{100} + 1{\cdot}43\,\mathrm{O} + 1{\cdot}257\,\mathrm{N} + \frac{2s}{100} + \mathrm{W} \text{ kilo.}$$

If the smoke-gases contain carbon monoxide and hydrocarbons, it must be remembered that, according to the formulæ $C + O_2 = CO_2$, $C + O = CO$, and $C + 2H_2 = CH_4$, each cubic metre of these gases contains 0·5395 kilo. carbon. If the analysis shows *k* per cent. carbon dioxide, *d* per cent. carbon monoxide, *m* per cent. methan, *h* per cent. hydrogen, *o* per cent. oxygen, and *n* per cent. nitrogen, as well as per cubic metre *r* kilo. carbon as soot, then 1 cubic metre of these gases contains—

$$\frac{(k + d + m)\,0{\cdot}5395}{100} + r \text{ kilo. carbon,}$$

and 1 kilo. of coal yields—

$$\frac{c\,\mathrm{C} : 100}{\frac{k + d + m}{100} \times 0{\cdot}5395 + r} = 1 \text{ cubic metre dry gases,}$$

in which we have—

$$\frac{\mathrm{G}\,k}{100} = \mathrm{K} \text{ cubic metre } CO_2, \frac{\mathrm{K}\,d}{k} \text{ or } \frac{\mathrm{G}\,d}{100}\,CO,$$

$$\frac{\mathrm{G}\,m}{100} \text{ methan, } \frac{\mathrm{G}\,h}{100}\,\mathrm{H}, \frac{\mathrm{G}\,o}{100}\,\mathrm{O}, \text{ and } \frac{\mathrm{G}\,n}{100} \text{ nitrogen.}$$

The proportion of soot is so trifling that it may be neglected.

Sulphurous or sulphuric acid and the vapour of water may be calculated as above, the weight of these gases being readily found with the aid of the following table:—

——	Specific Heat.	Weight of 1 Cubic Metre. kilos.	Specific Heat of 1 Cubic Metre.
CO_2 at 10° to 150°	0·2091	1·9781	0·414
200	0·2156	—	0·427
250	0·2220	—	0·439
300	0·2281	—	0·451
350	0·2341	—	0·463
1000	0·2891	—	0·572
1500	0·3180	—	0·629
2000	0·3290	—	0·651
CO	0·2450	1·2593	0·308
O	0·2175	1·4303	0·311
N	0·2438	1·2566	0·306
H	3·4090	0·0896	0·305
Steam	0·4805	0·8048	0·387
Methan (CH_4)	0·5929	0·7160	0·424
SO_2	0·1553	2·8640	0·445

The loss of heat by the higher temperature of the smoke-gases is found by multiplying the separate quantities of the gases by the specific heat and the excess of temperature of the gases above the air serving for combustion.

The loss from incomplete combustion is found from the combustion value of the unburnt coal in the cinders and the combustible ingredients, if any (carbon monoxide, methan, hydrogen, soot), of the smoke-gases.

As an instance of the loss of heat by the imperfect combustion of 1 kilo. of coal, the following figures may serve :—

——	Cubic Metres.	Kilos.	Combustion value. Heat-units.
CO	0·292	0·3680	893
Methan	0·073	0·0520	620
H	0·073	0·0065	187
Soot	—	0·0080	65
Carbon in cinders	—	0·0050	40
			1805

On the basis of the experience which the author has collected in more than 4000 gas analyses, he considers the apparatus figured and described above (Fig. 47) the best and the most convenient for judging of steam-boiler furnaces, domestic stoves, brick and porcelain furnaces, ultramarine furnaces, and alkali furnaces, and as also well adapted for examining blast-furnace and cupola gases, and of puddling furnaces; and even for examining the kiln-gases in sulphuric acid works, the saturation gases in sugar-works, and for petroleum lamps and gas engines. In order to determine the small quantities of combustible gases which occur in normal combustion-gases, even accurate volumetric procedures are generally insufficient. Those with platinum coils (Orsat), palladium-asbestos, &c., do more harm than good, as they lead to wrong conclusions. In such cases gravimetric determinations must be made with a sample drawn directly through the apparatus for a considerable time without the interposition of a gasometer. But at the same time a volumetric test should be made every five or ten minutes with the apparatus described above, in order to watch the progress of the combustion.

For gas fires the same apparatus is sufficient for ordinary control. Care must be taken that the generator-gases contain a minimum of carbon dioxide along with much carbon monoxide, whilst the gases escaping should contain a maximum of carbon dioxide and no monoxide.

Steam-boiler Firing.—By far the majority of steam boilers have too large a grate, and work, in consequence, with a great excess of air, losing much heat in the chimney.

The gases from a steam-boiler fire, for instance, contained 1·8 per cent. CO_2 and 19 per cent. O at 169°, representing a loss of heat of 3921 heat-units, or 60 per cent. of the total combustion value. After the masonry and the grate were thoroughly repaired, and the strength of the draught was regulated according to the indications of gas analyses, the gases contained 18·7 per cent. of carbon dioxide and 1·7 per cent. of oxygen, corresponding to a loss of heat of only 508 heat-units, or 7 per cent.! In judging a fire it is necessary to look *under* the grate; all the intervals between the bars must be equally bright.

For ordinary control it is sufficient to determine the CO_2 and O in three samples of the gas taken in rapid succession. The more CO_2 (without CO) is present, the better is the firing. For a coal fire 1·1 $k+o$ must be about 20, if the combustion is complete.

In large works it is advisable to connect a narrow lead pipe with the pipe fixed in the flue (inserting, however, a tuft of asbestos to keep back soot and dust), and to carry it into the laboratory. In order to take samples of gas at any time, so much gas is first drawn off as the pipes will hold, and the sample is then taken.

In conducting heating experiments (which, according to the importance of the case, should last from three to ten hours), six to twelve samples are taken hourly, determining their proportion of CO_2 and O, and of CO if present. If the gases contain notable quantities of the latter, which is the case only in defective boiler furnaces, the stoking must be altered, or samples of gas must be sealed up in bulbs and examined for carbon monoxide, hydrogen, and hydrocarbon. The moisture and the temperature of the air entering the fire-box should be determined hourly.

For deciding on the duty of a steam boiler by an evaporation experiment, which should be continued at least for ten hours, the Association of German Engineers and the Steam Boiler Association have agreed on the following regulations:—

Before beginning the experiments, the boiler must be cleaned, examined within and without, and tested for leakage; the flues are swept; the joints of the walls pointed and plastered over. The boiler must then be kept for at least one day in normal work, in order that it may be in its ordinary permanent condition.

The level of the water and the pressure of steam are accurately noted at the commencement of the experiments, and are kept all the time as uniform as possible. The pressure of steam is gauged by the manometer, and noted every fifteen minutes.

The feed-water is either weighed or measured in tared vessels, the contents of which are regulated according to the temperature. In accurate experiments weighing alone is admissible. The feeding must be effected regularly, and with a minimum of interruption; feeding must be avoided shortly before the beginning and the end of the experiment. The temperature of the water is measured in the cistern, from which it is drawn every thirty minutes, and just before its entrance into the boiler. This must be done with every feed. Feeding with injectors is permissible only when their supply of steam is drawn from the boiler in question.

If simultaneously with the examination of the performance of the boiler there is carried on an inquiry into the consumption of steam in a machine supplied by the boiler, the use of steam pumps for feeding is inadmissible if they derive their steam from the experimental boiler or if their waste steam comes in contact with the feed-water.

All leakage from the boiler fittings and all water blown off must be caught and taken into account. The weight of water thus ascertained must be recalculated as feed-water at 0° and steam at 100°. (*See* Table.)

In determining the consumption of water, care must be taken that the fire at the beginning of the trial is charged and cleaned normally, ash and slag being removed from the ash-box. If the ash cannot be removed, the residues therein should be brought to a given level before and after the experiment. The fire must be in the

same condition at the end of the experiment as at the beginning. The duration of the heating and the consumption of fuel are noted. The fuel consumed during the experiment is to be weighed and suitably broken up. The fire is fed regularly. Slags and ash are weighed and examined for the presence of combustible matter.

Experiments in which notable quantities of water have evidently been carried away mechanically by the steam are useless. No accurate and trustworthy methods are known for the determination of such water.

Evaporation experiments without a simultaneous examination of the smoke-gases have little, if any, value.

The total evaporation-heat of water is, according to Regnault, $= 606{\cdot}5 + 0{\cdot}305\ t$.

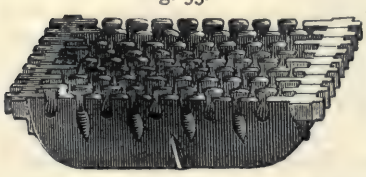
Temperature t of Saturated Steam.	Steam Tension		Pressure on 1 Square Centimetre in Kilos.	Evaporation-heat.
	in mm.	in Atm.		
0°	4·6	—	—	606·5
20	17·4	—	—	612·6
40	54·9	0·072	0·075	618·7
60	148·8	0·196	0·203	624·8
80	354·5	0·466	0·482	630·9
100	760·0	1·000	1·033	637·0
110	1075·4	1·415	1·462	640·0
120	1491·3	1·962	2·027	643·1
130	2030·3	2·671	2·760	646·1
140	2717·6	3·576	3·695	649·2
150	3581·2	4·712	4·869	652·2
160	4651·6	6·120	6·324	655·3
170	5961·7	7·844	8·105	658·3
180	7546·4	9·929	10·260	661·4
190	9442·7	12·425	12·834	664·4

Experiments executed by the author showed the following distribution of heat in three boilers :—

Coal to each square metre grate surface .	kilos.	123·8	86·3	46·9
Water to each square metre of heating surface	„	26·6	24·7	8·7
Combustion value of the coal determined calorimetrically	heat-units	7790	7720	7630
Percentage of heat taken up in water . .		74·9	68·4	83·6
Loss in cinders, &c.	per cent.	2·1	3·6	0·9
„ in gases imperfectly burnt . . .	„	—	—	0·3
„ in higher temperature of the smoke-gases	„	16·7	19·3	10·6
„ by conduction and radiation . .	„	6·3	8·7	4·6

The grate of the boiler furnace should be easily cleaned; hence all designs of grates which obstruct such cleansing with the object of giving the air free and uniform access to the fuel cannot be recommended—*e.g.*, that of Fletcher (Fig. 53). Those with lateral projections on the bars, the so-called polygon grates, are to be rejected. For fuel which does not cake, the oblique grates (*e.g.*, Tenbrinck) are worth attention, as here there occurs a partial degasifying of the fuel as it slides downwards, and thus the formation of smoke is to a great extent prevented.

Fig. 53.



This object is more perfectly effected by the so-called mechanical grates, which drive the fuel continuously into the fire-box, so that the gases evolved in front pass over the ignited coke and are burnt. One of the earliest arrangements of this kind is the chain grate. It is costly, soon wears out, and has been gradually abandoned.*

* We have observed that it brings out a considerable quantity of imperfectly burnt fuel, and lets it fall into the ashes, as waste.—[EDITOR.]

The arrangement of Dougal works well in practice.* All these devices, however, are expensive and consume mechanical power.

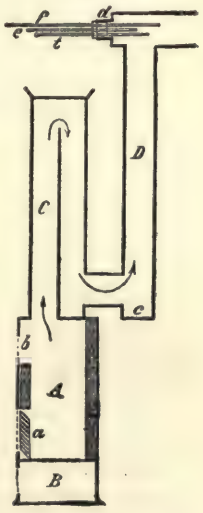
It has been already remarked that the almost numberless devices for "smoke consumption" are impracticable. Good gas-firing gets rid of smoke from the chimneys, but it cannot be recommended for steam boilers. The best solution of the important smoke problem is the substitution of coal-gas or water-gas burners for domestic fires, and of the gas engine for the steam engine. This latter step will probably be very generally adopted with the expiry of the Otto patent.† At Terni, near Rome, a mixture of water-gas and generator-gas is used for a gas engine. For the production of 14·35 horse-power the engine consumes hourly 11·86 cubic metres water-gas and 36·66 cubic metres generator-gas, and works very satisfactorily. This is, per horse-power—

0·83 cubic metre water-gas = 2182 heat-units
2·55 „ generator-gas = 2422 „

or about 4600 heat-units. The same work, if performed with lighting-gas, would require at least 0·9 cubic metre, representing 4770 heat-units. For producing the above-named quantities of water-gas and generator-gas 0·75 kilo. of coke or coal will be required, whilst for obtaining 0·9 cubic metre of coal-gas there would be consumed 3 kilos. of the best gas-coal (yielding only 1·8 kilo. of coke as residue), whilst a steam engine of the same power uses 4 kilos. of coals. There is besides the ease of distributing the power from gas engines, so that they may claim the future both for small and large industries.

House-heating.—The object here in view is to heat dwelling-rooms, &c., uniformly, with a minimum expenditure of fuel, and without rendering the air impure. Hence all kinds of heating which do not carry off the products of combustion are at once excluded—*e.g.*, the carbonatro stoves of A. Nieske, various coal-gas stoves, &c. Such arrangements testify to a marvellous thoughtlessness.

Fig. 54.



The forms of heating may be divided into *separate* arrangements (fires and stoves) and *collective* arrangements (heating with hot air, steam, or hot water).

Heating with open fires involves a great expenditure of fuel.‡ The open fire is used in Germany only where appearance is aimed at more than heating. The author cannot admit the alleged advantages of heating with radiant heat.§

Stove-heating is most common. To explain the action of an iron stove we may take the diagram, Fig. 54. The fire-box, *A*, ½ metre in height, is lined with fire-clay; the door to the fire-box, *a*, with an oblique grate, and that to the ash-pit, *B*, are fitted with screws, so that they may fit closely, as does also that through which fuel is introduced, *b*. The smoke-gases pass in the direction of the arrow through the top piece, *C*, and escape through the sheet-iron pipe, *D*, to the chimney.

At the aperture, *d*, the thermometer, *t* (filled with nitrogen), is inserted for experimental purposes by means of a good cork, the tube, *e*, leading to an apparatus for

* *Dingler's Journal*, 232, p. 346.

† Before coal-gas is used in the household it must be much cheaper, and before water-gas can be safely introduced to warm our houses and cook our food it must be freed from carbon monoxide, as already described.—[EDITOR.]

‡ Ninety per cent. of the heat generated being wasted. The recent "improvements" introduced in England have been steps in the wrong direction.—[EDITOR.]

§ *Jahresber.* 1887, p. 145.

measuring the draught and the glass tube, *f*, which is connected with apparatus for the analysis of the smoke-gases. These are thoroughly mixed by the bendings through which they pass, so that specimens taken simultaneously at *c* have the same composition to $\frac{1}{10}$ per cent. If anthracite is used, the gases have the composition given in the subjoined tables.

The results indicate a total loss of heat in the chimney of only 8 per cent., so that 92 per cent. of the heat remains in the room.

To obtain such favourable results the fire-room of all iron stoves must be lined with fire-proof stone, or tiles of fire-clay. If the fuel touches the iron surfaces, complete combustion is rarely possible. Further, the iron plates become overheated, so that they allow carbonic oxide to permeate them, and they certainly singe all organic dust, thus spoiling the air of the room. It would be desirable for the gases to descend again in order to give off their heat still more completely through the sides of the stove to the air of the room.

Time. h. m.	CO_2.	CO.	O.	N.	Temperature of Escaping Gases.	Remarks.
2.50	12·5	—	8·0	79·5	240°	Temperature in the laboratory, 12°.
3.00	12·6	—	7·9	79·5	241	1 millimetre draught.
3.10	11·5	—	9·1	79·4	240	Fuel added, doors *a* and *b* closed.
3.20	11·8	trace	8·4	79·8	201	
3.30	13·7	—	6·4	79·9	234	
3.40	14·1	—	6·2	79·7	242	
3.50	13·6	—	6·7	79·7	248	Fuel added.
4.00	13·5	—	6·9	79·6	206	
4.10	13·4	—	7·2	79·4	229	
4.20	13·5	—	7·0	79·5	248	
4.30	13·1	—	7·4	79·5	247	
4.40	12·0	—	8·6	79·4	246	

If the stove is used full, the lower doors must be kept tightly closed, as otherwise carbon monoxide may be formed, which, if the draught is defective, may pass out into the room. The regulation of the supply of air is very important for the utilisation of the heat. If, in the stove Fig. 54, the ash-pit door is opened, so that the air passes through the horizontal grate into the fire-box, and also the door *a*, the temperature of the escaping gases rises so rapidly that the thermometer has to be removed, whilst, in accordance with the increased draught, the proportion of carbon dioxide falls, and the loss of heat rises up to 40 per cent.

Hundreds of thousands of stoves in Germany which have imperfect doors or none at all allow from 50 to 80 per cent. of the entire combustion value of the fuel to pass up the chimney, a loss which amounts yearly to millions of marks.

Certain stoves, such as those of Sturm and Henschel, are not used or known in Britain, and their description may therefore be omitted.

Earthenware stoves are generally built up of tiles. A Russian stove, *e.g.*, is a longish rectangular block, and has six smoke channels. Fig. 55 shows the plan, Fig. 56 an elevation of the broad side, Fig. 57 of the narrow side, and Fig. 58 a longitudinal section. From the fire-box covered with an arch, *a*, the fire rises up in the flue 1, descends again in flue 2, rises in 3, falls in 4, rises in 5, and falls in 6, whence it escapes through the stove-pipe into the chimney. Near the connection of the last flue with the stove-pipe a four-sided plate of cast iron (Figs. 59, 60, and 61) is built in; this plate has in the middle an aperture of 21 to 24 centimetres in diameter, with an upright neck of 3 centimetres and an internally projecting margin of 2 centimetres. A cast-iron cover, *a*, provided with a handle, fits over the aperture, a second, larger, cover, *b*, with a projecting margin, fits over the neck and closes the whole. For heating, the fire-box is filled with short pieces of wood, the wood is kindled, the door

being left open at first; it is afterwards closed so that the air enters through its apertures.

Experiments which the author carried out with a tile stove, 1·2 metre wide and 3 metres in height, showed that with a coal fire from 40 to 80 per cent. of the heat escaped up the chimney, so that tile stoves are less suitable for giving out heat than iron stoves. The surfaces which come in contact with the air of the room are kept carefully free from sharp angles and roughnesses, and are covered with a glaze, all circumstances which impede the communication of heat as much as possible. Hence the

Fig. 55.

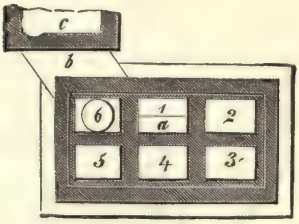


Fig. 56.

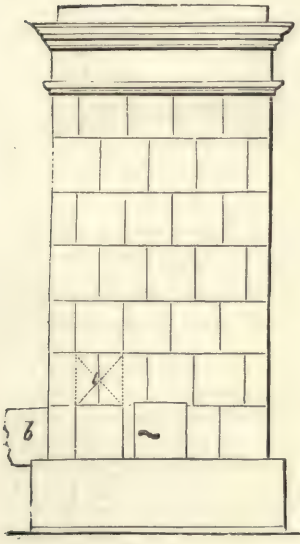


Fig. 57.

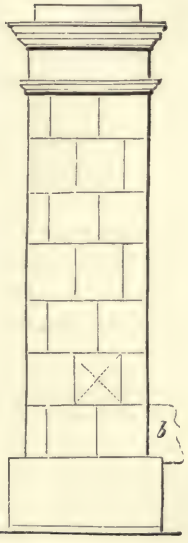


Fig. 58.

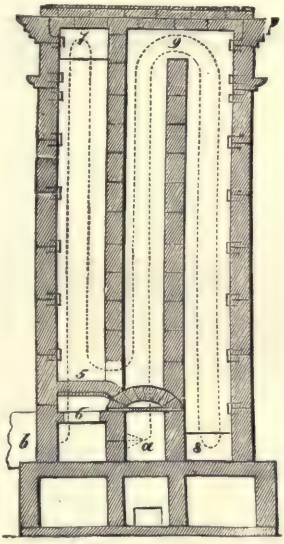


Fig. 59.



Fig. 60.

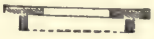
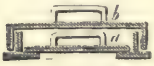


Fig. 61.



gases pass into the chimney with about 100° more heat than that from the iron stove (Fig. 55), the surface of which is covered with small ornaments in relief, and is consequently well adapted for throwing off heat.* The loss of heat in tile stoves can be diminished by carefully closing the doors. If the supply of heat to an iron stove lined with fire-clay or tiles is properly regulated it retains the heat as long as a tile stove.

Hot-air heating differs from stove heating by the circumstance that the fire is not in the rooms to be heated, but outside, and often below them. As a specimen of a successful arrangement of this kind the author describes that existing in his own house. It has to supply six rooms with warm, pure air—below, three dwelling-rooms, *A*, *B*, *C* (Fig. 62); *V*, an ante-room; *D*, kitchen; above, one storey high (Fig. 63), *A*,

* Tile stoves can of course be made with unglazed surfaces and small projecting ornaments.

library; *C*, work-room; *D*, laboratory. The heating arrangements are in the space below *B*.

The air-entrance, *K* (Figs. 64–68), is underneath the veranda, on the south-western

Fig. 62.

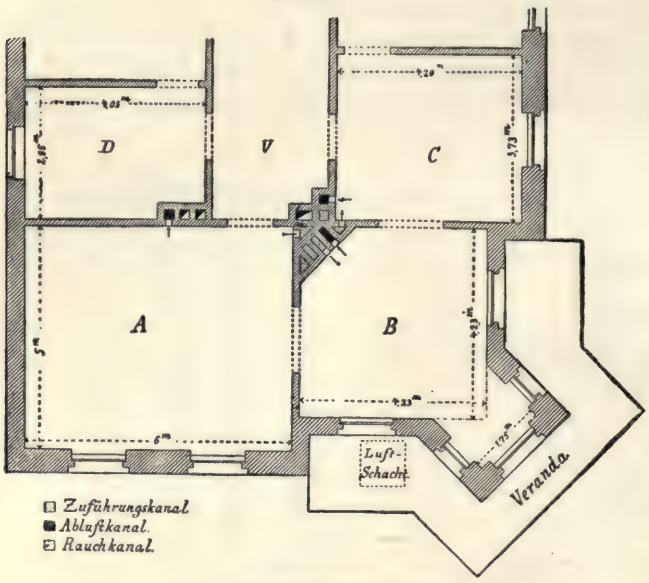


Fig. 63.

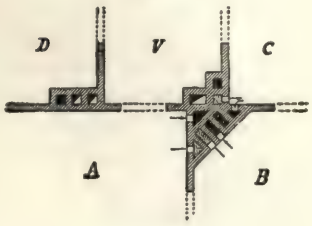
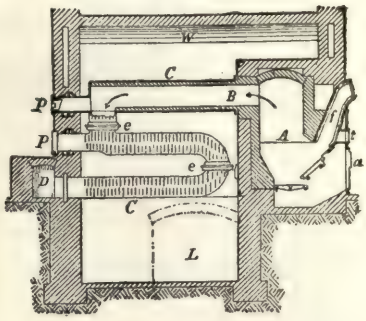


Fig. 64.



Explanation of Terms.

Zuführungskanal	Access for air.	*Rauchkanal*	Smoke channel.
Abluftkanal	Exit for air.	*Luftschacht*	Air shaft.

side of the house. The opening is covered with a wire grating, before which stands a triple row of juniper bushes, so that all the coarser impurities are kept out.

The air-filter, *F*, is 2 metres wide, and has a total filtering surface of 50 square metres. The arrangement is adapted for 5000 cubic metres air per hour, whilst the

Fig. 65.

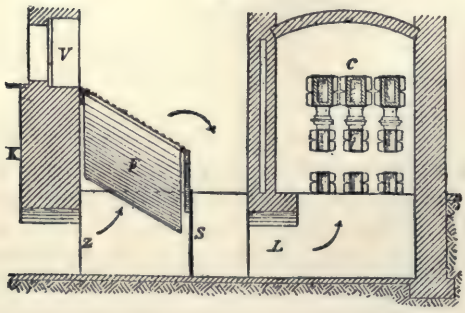
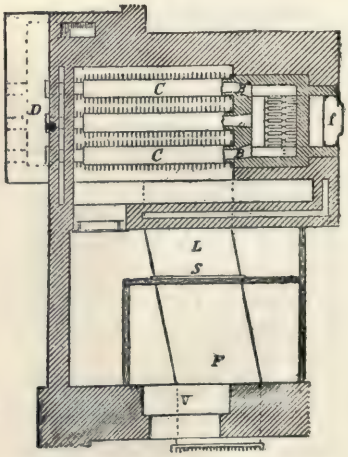


Fig. 66.



heating itself requires only 2000 to 3000. Not the least disturbing influence has been felt in the supply of air in three years. All the air entering has to pass through a dense cotton tissue, which keeps back soot and dust. The air, freed from dust, passes

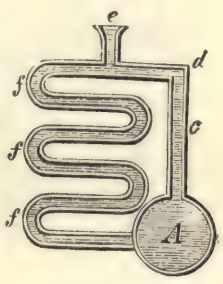
through the channel, *L*, into the heating-room, becomes warmed in the tubes, *C*, and passes at *W* into six vertical channels of smooth masonry (but not plastered), of which five, as shown in Figs. 62 and 63, are placed in a niche of the corner room, and open into the rooms 2 metres above the floor. From here the waste air escapes through six shafts close above the floor. Coal is introduced at *f*, whilst the door *t* is opened only to stir the fire; the door *a* regulates the supply of air.

About 85 per cent. of the total combustion-value served to warm the rooms, and 5 to 7 per cent. more are not wasted, but serve to warm the staircase uniformly.

The greatest consumption of fuel in twenty-four hours was 110 kilos. of coal at an outside temperature of $-15°$ and a violent east wind with driving snow. At $+3°$ and calm weather only 25 kilos. of coal were used. The objections raised against hot air on the score of drying the air are completely groundless.

Water-heating.—As is shown in the diagram, Fig. 67, the water heated in the boiler, *A*, rises in the tube, *c*, up to *d*; it becomes heavier again by giving off its heat in the pipes, *f*, laid down in the rooms, &c., to be heated, and flows back to the boiler. If the system of pipes is left open at its highest point, *e*, no increase of pressure can ensue, and we have a low-pressure water heating; if the system is closed so that the water may be heated to 180°–200° (Perkins' tubes), it is a high-pressure water heating. In the latter case the pipes may be smaller, but there is the possibility of an explosion. The warm water of artesian wells and that of hot springs is used for heating conservatories, factories, &c. The Catholic town church at Baden-Baden has been heated since 1867 by means of the hot springs in the neighbourhood, which have a temperature of 67°.

Fig. 67.



Steam heating may be effected either at low pressure ($\frac{1}{2}$ atmosphere) or at high pressure. In each case the steam passes into mains laid beneath the floors of the buildings to be heated. Here it is liquefied by giving off its latent (and a part of its specific) heat, and flows back to the boiler.

All collective heating arrangements have the great advantage, as compared with stoves and open fires, that they occasion no ash, soot, &c. They allow also of a great economy of labour, as only a single fire has to be kept up to warm a great number of rooms. They also admit of a more perfect utilisation of the fuel than do ordinary stoves, and they enable a uniform and unchanging temperature to be kept more easily than does any other kind of firing.

Hot-air heating involves the least initial outlay, is easily attended to, and, where the ventilation is good, it produces a uniform heat in the rooms. It is not adapted for distributing heat horizontally in large halls or long series of rooms, since hot air should ascend vertically as nearly as possible. In such places steam or water heating is preferable.*

Heating with Coal-gas.—This is a very pleasant, but a very expensive, arrangement. 1 cubic metre coal-gas evolves 5300 heat-units, watery vapour being one of the products of combustion. Of this total, about 5000 heat-units are utilised. For a small room during the entire winter the average demand for heat is 10,000 heat-units daily. This requires 2 cubic metres of coal-gas, which may cost, according to the locality, from

* Hence steam or hot water is selected for heating museums, libraries, galleries of pictures, conservatories, &c., where a uniform heat, strictly under control, is required in all parts. It must be remembered that the mains should never be allowed to lie upon wood, still less sawdust, shavings, &c., as, though the temperature may never exceed 100°, wood thus heated gradually undergoes a series of chemical changes which render it spontaneously combustible. The mains should be supported upon firebricks.—[EDITOR.]

0·24 to 0·40 shilling, whilst in properly arranged hot-air heating the coal consumed costs merely 0·03 to 0·04 shilling. In heating with stoves we have, on the other hand, the trouble of feeding the fires, the inevitable dirt, and the difficulty of maintaining an even temperature.

Gas-firing.—Gas-firing is distinguished from ordinary firing by the circumstance that the fuel is first gasified, and then burnt, atmospheric air being introduced at two distinct places. The air required for gasifying enters the fuel through the grate. The air (called secondary) needed for burning the gas thus formed enters the fire-box.

A system of gas-firing adapted for lignite is shown in Figs. 68 and 69. In this

Fig. 68.

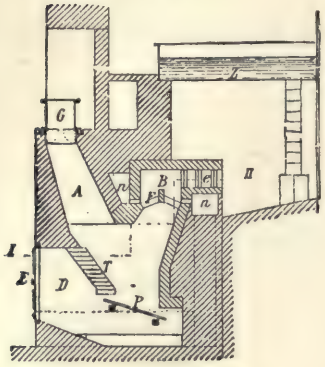
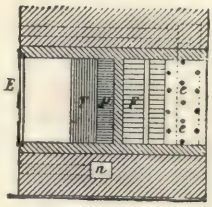
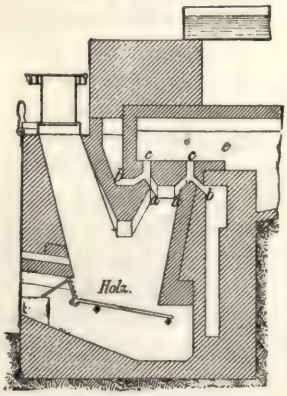


Fig. 69.



Sections I–II.

Fig. 70.



Holz—Wood.

arrangement, built by Heupel at the Aussee Saltworks, the boiling pans, *Z*, are 17·1 metre long by 7·6 broad, so that each has a heating surface of 130 square metres, for which three gas generators, *A*, with the grates, *T* and *P*, were placed equally distributed over the breadth of the pan. The regulation of the production of gas is effected by means of tightly fitting air-valves in the door, *E*, in front of the ash-pit. The apparatus for burning the gas, which is separated from the feeding shaft, *A*, by means of a simple vault, consists of an almost horizontal grating, *F*, constructed of fire-bricks, and of the vertical grating, *e*, between which is the true fire-box, *B*, and in which vent the air-passages, *n*, are introduced in the side walls of the generator. The gases evolved in the generator pass through the grating, *F*, into the fire-box, *B* (closed above), where they mix with the air warmed against the stove sides and streaming in from the air-channels, *n*, and are ignited.

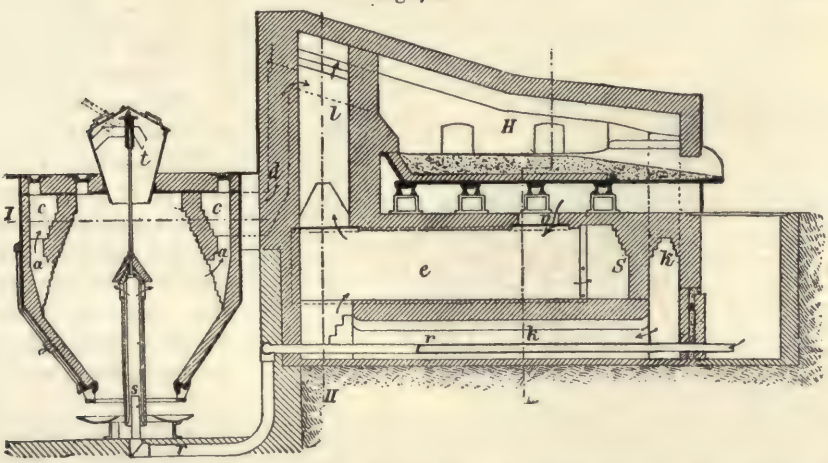
The forms of burners by which a perfect combustion is effected are shown in the wood-gas stove, Fig. 70.

If the generator does not stand directly under the fire-box, as in that of Boetius (Fig. 36), gas-firing involves a loss of heat. As compensation, the combustion-air, more rarely the air for gasification, is strongly heated by the waste heat.

C. W. Siemens effects the formation of gas in the generator by means of heated air (Fig. 71). The fuel is introduced by the hopper, *t*; the gases are carried off through a great number of channels arranged round the stove, and arrives at the ring-shaped draught, *c*, which, as is shown by dotted lines and arrows, leads through *d* to the furnace. The gases meet with the air rising from the regenerator pipes through the channel *l*, and burn. After the flame has completed its work in the heating space of the furnace, it passes out opposite to the entrance through apertures which lead the gases through the channels *k*, to the regenerator flues, *e*, whence they ultimately arrive at the chimney, *S*. The air required for the combustion of the gases arrives at the regenerator through the openings, *v*, which lead to *o*, which in turn is in connection

at the other end with the channel *l*, already mentioned. A part of the air coming from the regenerator flues may be led to the generator in order to volatilise the fuel there, or, as shown in the figure, the air needed for this purpose may be heated in

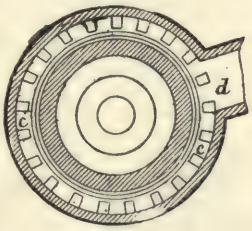
Fig. 71.



separate tubes which lead to a blast, *s*, at the foot of the generator. The ashes, &c., fall into a reservoir of water at the foot of the generator. The steam thus produced enters the gas generator, where it is decomposed on contact with the ignited coal, and serves to enrich the gases.

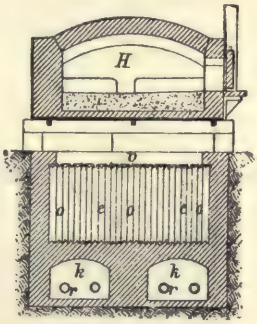
The preliminary heating of the air for gasification may be objectionable in so far as it raises the temperature in the gas generator, and thus increases the action of the slag upon the masonry. It is of value only when the generator-gases enter the fire-box at a high temperature.

Fig. 72.



Section I.

Fig. 73.



Section III.

The preliminary heating of the air for combustion is of much greater importance. It is effected according to the procedure of Fr. Siemens by passing the combustion-gases which leave the furnace at a high temperature through a grating of stone (regenerator), and then inverting the current and causing the air for combustion to ascend through the ignited stones. According to another process the heat of the combustion-gases is transferred to the ascending air by partition walls (Figs. 72 and 73).

Fig. 74.

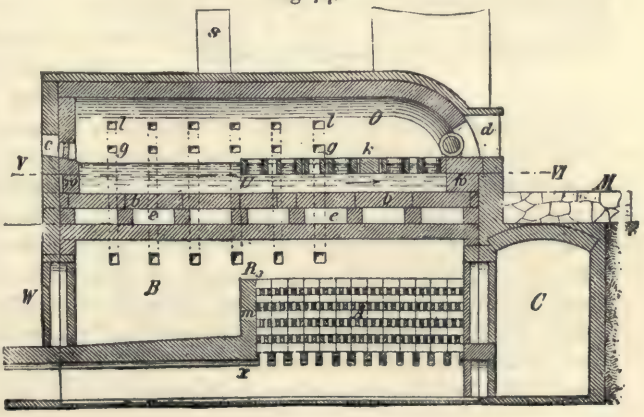


Fig. 74 shows a longitudinal section through the trough and the regenerator of a Siemens glass-melting furnace provided with regenerators of the first kind. Fig. 75 shows a horizontal section on *V*, *VI*, and Fig. 76 a transverse section on *VII*, *VIII*, through the entire furnace, and Fig. 77 the section of a work-place. The four regenerators, R_1 to R_4, lie close alongside each other, and form a connected whole with the furnace, thus reducing the loss of heat by radiation and conduction. The greater part, *A*, of the regenerators is lined with fire-stones, but not the smaller portion, *B*, separated by the wall, *m*. This part, situate next to the place for introducing the materials, takes up the constituents of the charge, so that the regenerators, *A*, remain clean; these are easily accessible from *C*, as are the parts *B* from the alternating valves, *W*. The trough itself is an entire whole, in consequence of which repairs are seldom needed. In the melted glass there float at the end of the furnace turned towards the work-places, *a*, rings of stoneware, whilst the flame sweeps through the upper part, *O*, of the furnace, so that the melting of the glass takes place on the surface only. The bottom, *b*, and the sides, *w*, of the trough are, as formerly, surrounded with air refrigerators, *e*, in which a brisk current of cold air is kept up by means of the chimneys, *s*. The trough is thus not only better preserved, but the glass is prevented from passing through the joints.

Fig. 75.

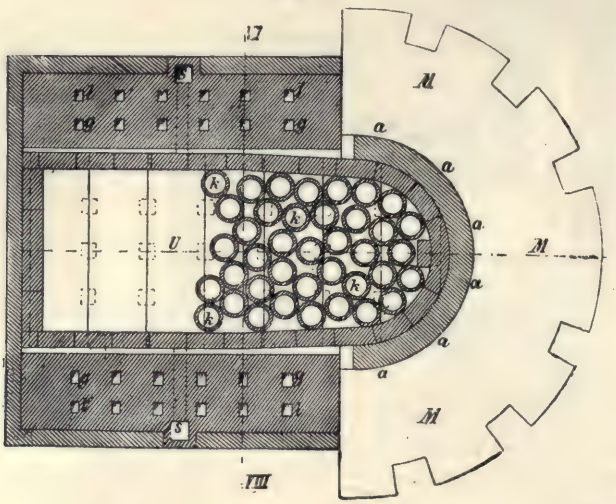


Fig. 76.

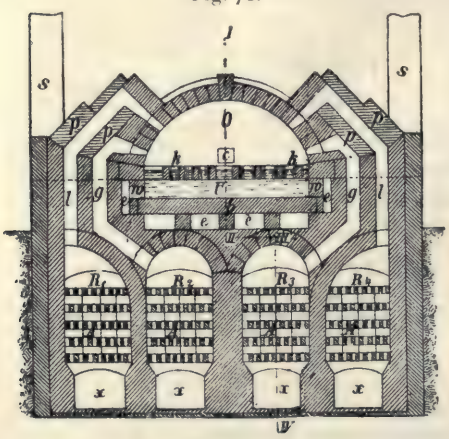
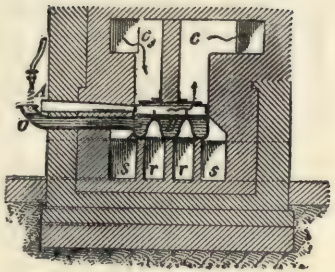


Fig. 77.



As a good instance of the second method of obtaining heat from the combustion-gases we may take the so-called Munich generator furnace of N. H. Schilling (Figs. 78 to 82). The heat necessary for gasifying the coke enters the aperture, *A*, which can be regulated with a slide, and mixes with the watery vapours rising up from the box, *B*. The gaseous mixture traverses the channels *c* to c_3, is heated by their sides, which in turn are heated by the escaping smoke-gases, passes under the grate, *D*, and through the ash-pit, *w*, into the burning stratum of fuel. The generator-gases formed pass through the channel *F* to the furnace, and meet in the burners, *G*, with the air previously heated. The combustion-gases traverse the retort furnace in the direction of the arrows, leave it at the end of channel *z*, and enter into the regeneration system. The hot gases pass through channels *o* to o_3, which lie between the channels

Fig. 78.



Section IX-X.

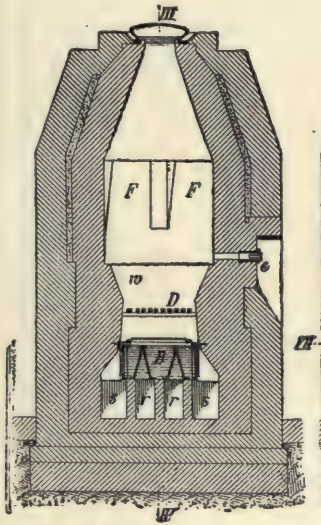


Fig. 79.
Section I-II.

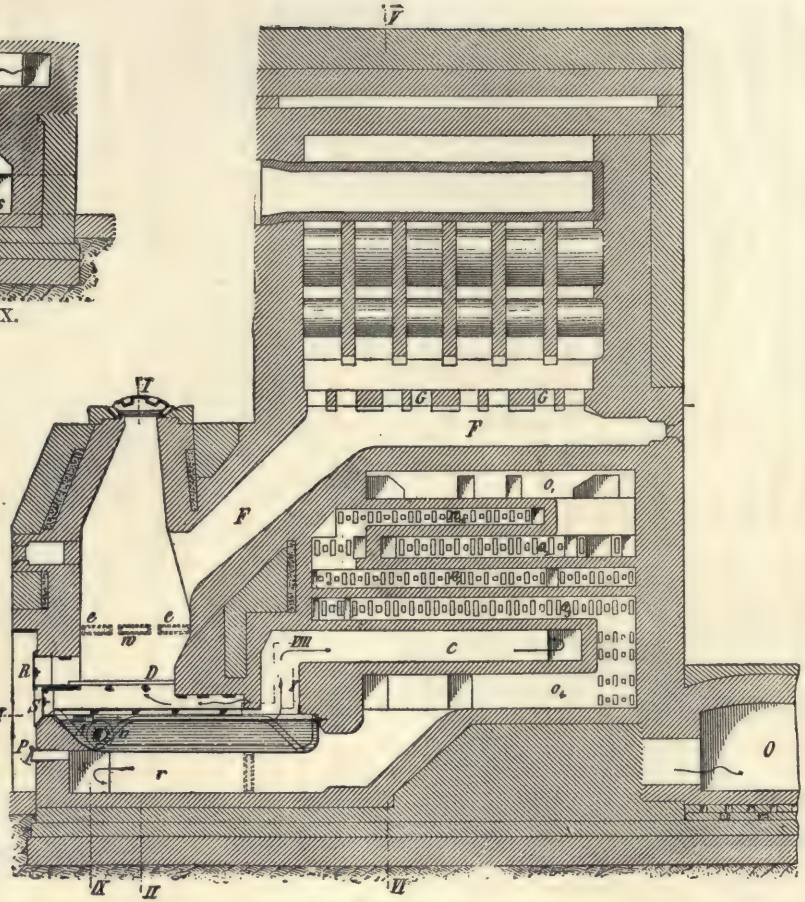


Fig. 80.
Section III-IV.

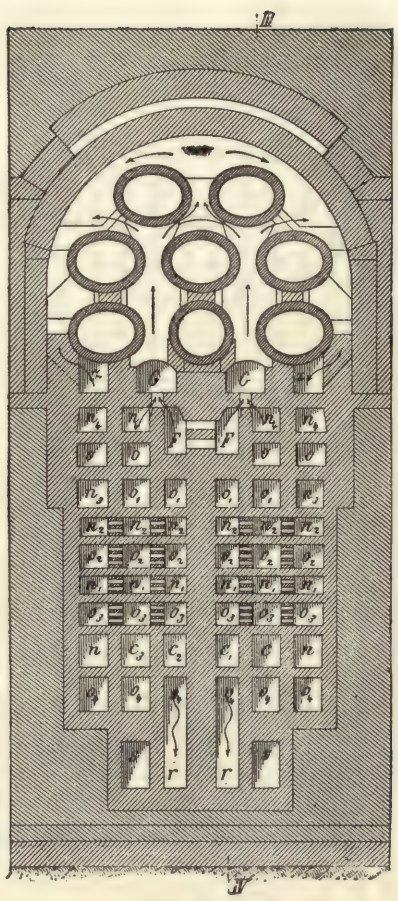
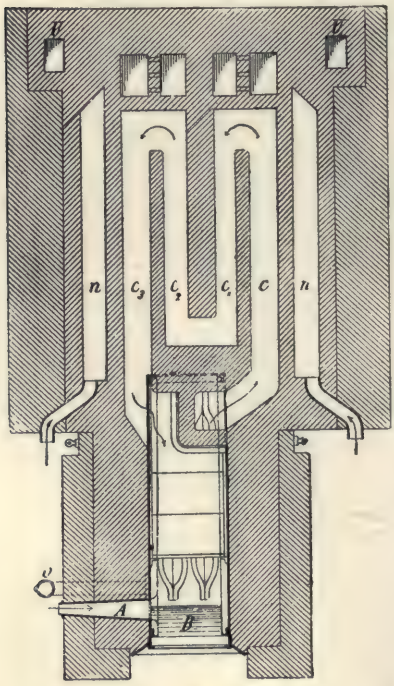


Fig. 81.
Section V-VI.

n to n_1, for warming the combustion-air, then through channel o_4, the walls of which heat the mixture of gas and watery vapour passing to the generator, arrive under the water-cistern, B, at r, and through s into the smoke-pipe, O.

Fig. 82.



Section VII–VIII.

For more rapidly transferring the heat from the smoke-gases to the air moving towards the furnace, and for securing the structure and tight joints of the so-called regeneration, the several channels are traversed by perforated stones, which increase the heating surface. The slide for regulating the draught in the chimney is behind the regeneration, not behind the furnace. The heating surface of the water-tank beneath the generator is arranged so that the quantity of steam which is sufficient for all cases, 1000 to 1300 kilos., may be produced, thus completely preventing the formation of slag. To regulate the quantity of steam produced there is provided a valve, P, which can be set at pleasure, thus moderating the temperature. If, on using coke with from 14 to 16 per cent. of ash, the ash-pit has become filled in about thirty-six hours with the residues of combustion, they are removed as follows:—Through the openings, e, which are in general tightly closed, there are thrust iron rods to catch the fuel in the generator. The covers, R and S, are removed, and the ash fallen upon the grate is taken away. All the apertures for cleansing are closed again. The water which has evaporated from B is renewed by a continual flow from v; an overflow removes any superfluous water. In order, when setting the furnace in action, to remove temporarily the regeneration there are connecting channels, U, through which the smoke-gases may be passed at once to the chimney.

Such furnaces have been in regular work at the Munich Gasworks since 1881. Three series of observations, of several months each, gave the following results:—

Yield of gas in twenty-four hours	2300 cubic metres
Coal distilled in twenty-four hours in eight retorts	7350 kilos.
Coke consumed per furnace in twenty-four hours	800 „
Yield of gas per retort in twenty-four hours	287 cubic metres
Gas per furnace and charge in four hours	383 „
Gas from 100 kilos. of coal	31 „
Coal distilled per retort in twenty-four hours	919 kilos.
„ „ „ and charge	153 „
Consumption of coke (14 per cent. ash) per 100 kilos. of coal distilled	10·9 „
Consumption of coke (14 per cent. ash) per 100 cubic metres of gas	45·8 „

The generator-gases contain as a mean 8·6 per cent. of carbon dioxide, 20·6 of carbon monoxide, 15 of hydrogen, and 55·8 of nitrogen. They enter the furnace at about 1150°. The combustion-gases contain 17 to 19 per cent. of carbon dioxide, about 2·5 per cent. of oxygen or small quantities of carbon monoxide. They leave the furnace at about 1400°. After having traversed the flues o to o_3, and given off a part

of their heat to the air ascending in the intervening channels, they still have a temperature of 900°, whilst the combustion-air arriving at the furnace before entering the channels m to m_4, has become heated to 1000°–1100°. Passing further down, the smoke-gases play round the channels c to c_3, and heat the air passing to the generator to 350°; finally, on passing through the channels r, they produce the steam employed in the generator, and enter the chimney at about 550°.

An exit temperature of 1400° without regeneration would represent a loss of 64 per cent. of the heating value of the coke; but by the regeneration process the smoke-gases are cooled down to 550°, and the loss is reduced to about 25 per cent. The heat thus recovered is conveyed back to the furnace, 20 per cent. by the heated combustion-air, 6 per cent. by the preliminary heating of the generator-air, about 5 per cent. is used in evaporating water, whilst the rest is lost by conduction and radiation outwards.*

This latter way of recovering heat has the advantage that the direction of the draught does not require to be changed every fifteen or thirty minutes. Care must be taken that the divisions between the channels for air and combustion-gases are air-tight, so that no disturbing intermixtures take place. This point has to be determined by the analysis of samples of gas taken from channels n_4, z, and r.

Gas-firing gives satisfaction in metallurgy, in glass manufacture, and in burning clay and cement.

In industrial heating operations, the dissociation of the gases of combustion is without importance.

LIGHTING-GAS.

History.—As far back as 1727–1739, Clayton, Bishop of Cork, and Dr. Hales observed the escape of gas on heating coal.† In 1767, Dr. Watson, Bishop of Llandaff, observed that combustible air could be conveyed through pipes. Pickel, Professor of Chemistry at Würzburg, lighted up his laboratory in the gardens of the Julius Hospital with gas obtained from bones, in 1876. About the same time Dundonald made experiments at his country seat of Culross Abbey on lighting with coal-gas. The first question for him had been the production of gas-tar as a by-product of the coke manufacture. The workmen fixed iron tubes in the condenser in which the tar was deposited, and kindled the escaping gas for light in the night. Strictly speaking, the beginning of gas-lighting took place in 1792, when Murdoch lighted his house and works at Redruth, in Cornwall, with gas obtained from coal. His process did not become known on the Continent until about ten years subsequently; hence the French claim the invention for their countryman, Lebon, who in 1801 illuminated his house and garden with gas produced from wood. The enterprise proved a complete failure, on account of the feeble illuminating power of wood-gas, and was soon abandoned. The first gas illumination on the large scale was installed by Murdoch in 1802, at the works of Watt & Boulton, the Soho Foundry, near Birmingham. In 1804 he fitted up a similar installation at a cotton-spinning establishment in Manchester.‡ From this time the use of gas became extended. But for some time it was confined to factories. Its introduction into daily life dates from 1812, when the streets of London were lighted with gas. In 1824 gas-lighting was introduced into Hannover, and other continental cities followed the example. The wood-gas introduced at Pettenkofer's suggestion into Munich and other South German cities has probably been everywhere

* *Dingler's Journal*, 248, p. 27.

† Indeed, in 1659 Thomas Shirley is said to have ascribed the burning exhalations from the well of Wigan to the subjacent coal-beds.

‡ Winzer, who converted his name into Winsor, is sometimes regarded as a discoverer of gas-lighting, but he was merely the inventor of gas companies.

abandoned in favour of coal-gas. For small installations oil-gas and resin-gas are convenient, as they require little purification.

For the production of lighting-gas, coal is heated to whiteness in retorts, formerly made of cast-iron, but latterly of fire-clay. As the source of heat, the residual coke is used, being formerly burnt in common grates. During the last ten years the firing has been improved, so that the consumption of fuel has been reduced one-half. In the half-gas-firing of J. Hasse and M. Vacherot the fuel is introduced (Figs. 83–85) through

Fig. 83.

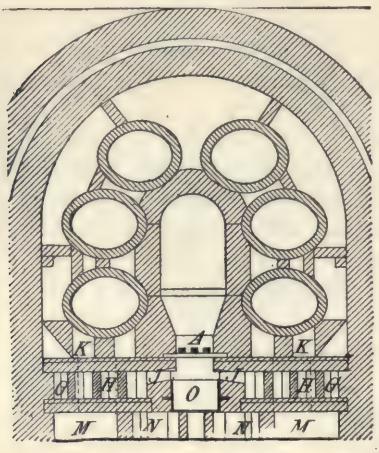
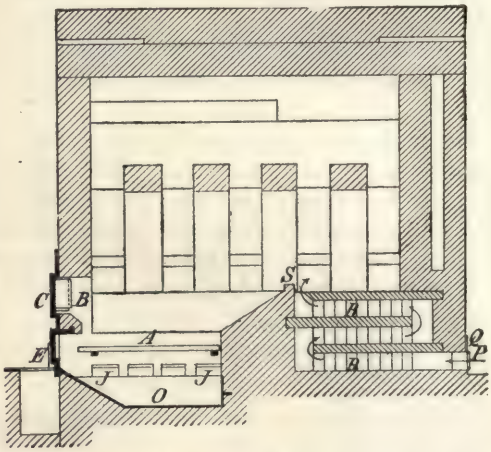
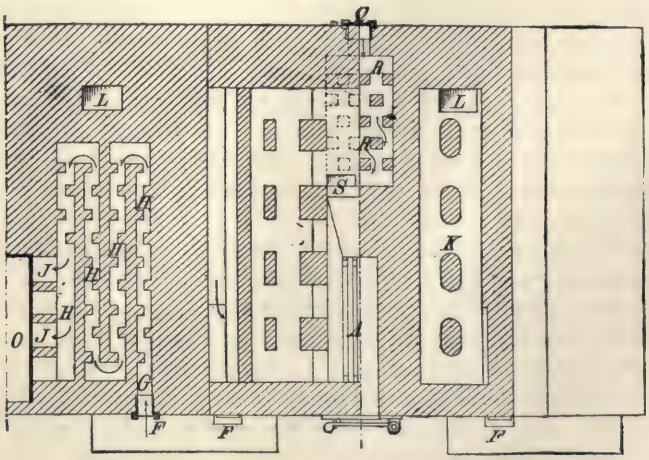


Fig. 84.



an opening, *B*, provided with a tightly fitting door and laid upon the grate, *A*. Slags and ashes are removed through the air-tight door, *E*. When both doors are closed the combustion-air, regulated by the slide, *F*, into the furnace right and left at *G*, traverses the channels in the direction of the arrows, and passes through the slit *J* to the left and right under the grate. Where circumstances permit, air can also be introduced under the flues *M* and *N*, and conveyed from thence to the channels *H*. The products of combustion, after they have passed uniformly through the furnace, enter the smoke flue, *K*, from before backwards, downwards in *L*, in *M* from behind forwards, and in *N* in the reverse direction to the chimney. In this manner the products of combustion give off a great part of their heat both to the air entering through the air-channels *H*, and to evaporating the water in the tank, *O*, under the grate. As the fuel is packed high up on the grate and maintained at the same height, a complete combustion does not take place, but there is formed a considerable percentage of carbon monoxide, for the combustion of which a further supply of air is needful. This secondary combustion-air enters from the back of the furnace at *P*, where its access is

Fig. 85.



regulated by the slide, *Q*. It traverses the air channels, *R*, in the direction of the arrows, and arrives through the slit *S* in contact with the gases coming from the combustion hearth. The channels *R* are heated by radiation from the surrounding masonry. The channels *H* may be connected with the channels *R* in such a manner that the air passes through *H* into *R*.

Fig. 86.

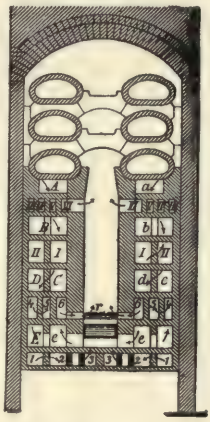
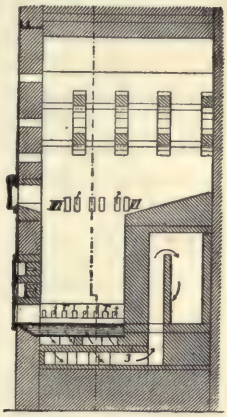


Fig. 87.



In the retort furnace of Stedman, provided with a gas-firing, the combustion-gases, as shown in Figs. 86 and 87, pass from *A* to *E*, or from *a* to *e*, down into the chimney. The air for gasification enters on both sides at *J*, traverses the channels, 1 to 6, and enters into the bed of coke at *r*. The air for combustion enters at *I*, passes through *II* to *V*, and meets with the generator-gases at *VI*.

The furnaces of Liegel and Klönne, in which the generator is built into the furnace, have given satisfaction in practice.

The furnaces of Hasse and Didier have much similarity with the Munich furnace. The air for gasifying enters at *P* (Figs. 88 and 89), and is warmed in channels left in the masonry of the generator outside the furnace. The air for combustion entering at *S*, rises in the channels, *o*, whilst the products of combustion pass from the furnace down through the channels, and yield the heat necessary for producing steam in the tank, *D*. The steam passes under the grate of the generator.

Fig. 88.

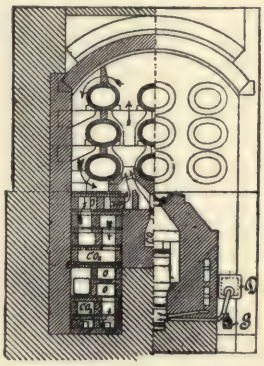
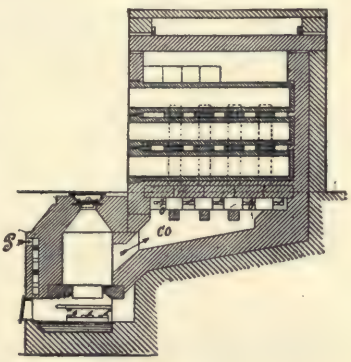
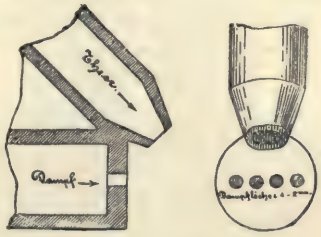


Fig. 89.



Tar-firing.—In consequence of the reduced value of tar and its products, it is in many gasworks advantageous to use it as fuel. Tar has a combustion-value of 8500 to 9000 heat-units, and is blown into the fire in a state of fine division by compressed air and steam. Körting's pulveriser (Fig. 90) allows the steam to issue from four apertures of 1 mm. in diameter. At a pressure of 3 atmospheres these apertures let pass 5·4 kilos. of steam, pulverising 30 kilos. of tar. At the exit the steam takes the temperature of 100°, is heated to the temperature of the furnace, gives up heat to the retorts, and leaves the furnace at about 1000°. It thus occasions a loss of heat corresponding to the rise of temperature from 100° to 1000°, *i.e.*, 900°. Steam has a specific heat of 0·475—*i.e.*, to heat 1 kilo. of

Fig. 90.



Theer—Tar. *Dampf*—Steam.

steam to 1°, 0·475 heat-unit is needed. To heat 5·4 kilos. to 900° there are needed $5·4 \times 900 \times 0·475 = 2308·5$ heat-units. From the 30 kilos. of tar burnt in this time there are produced 260,000 heat-units, so that the loss as steam does not come to 0·9 per cent. At the Hannover Gasworks 100 kilos. of coal are degasified along with 13·5 kilos. of tar. Sometimes tar is let flow into the generator.

As already mentioned, the composition of the volatile matter given off on heating coal fluctuates greatly. The Paris Gas Company experimented at their works at La Villette with fifty-nine kinds of coal, and very carefully with twenty-three of the same, using 36 tons of each.

The nitrogen was not determined, but assumed as 1 per cent. in each case; all the coals were grouped in five classes.

		I.	II.	III.	IV.	V.
Composition of coal.	Oxygen	5·56	6·66	7·71	10·10	11·70
	Hydrogen	5·06	5·37	5·40	5·53	5·64
	Carbon	88·38	86.97	85·89	83·37	81·66
	Nitrogen	1·00	1·00	1·00	1·00	1·00
		100·00	100·00	100·00	100·00	100·00
Products of distillation.	Moisture per cent.	2·17	2·70	3·31	4·34	6·17
	Volatile ,,	26·82	31·59	33·80	37·34	39·27
	Coke ,,	73·18	68·41	66·20	62·66	60·73
Ash in	Coal	9·04	7·06	7·21	8·18	10·73
	Coke	12·35	10·32	10·80	13·05	17·76
100 kilos. of coal yield	Gas cubic metres	30·13	31·01	30·64	29·72	27·44
	,, kilos.	13·70	15·08	15·81	16·95	17·00
	Coke ,,	77·81	74·70	72·31	68·96	67·36
	Tar ,,	3·90	4·65	5·08	5·48	5·59
	Ammoniacal liquor ,,	4·59	5·57	6·80	8·61	9·86

The gas, on a very imperfect examination, showed—

	I.	II.	III.	IV.	V.
Carbon dioxide	1·470	1·580	1·720	2·790	3·130
,, monoxide	6·680	7·190	8·210	9·860	11·930
Hydrogen	54·210	52·790	50·100	45·450	42·260
Methan + nitrogen	34·370	34·430	35·030	36·420	37·140
Benzoles	0·790	0·990	0·960	1·040	0·880
Other gases absorbed in bromine	2·480	3·020	3·980	4·440	4·760
	100·000	100·000	100·000	100.000	100·000
Specific gravity	0·352	0·376	0·399	0·441	0·482
Required per carcel litres	132·100	111·700	103·800	102·100	101·800

The Scottish cannels, the Boghead minerals, which produce no residue applicable as fuel, and the Australian kerosene shales, which likewise leave no coke on distillation, are almost exclusively used at gasworks to improve the gas from common coal, and are added in proportions varying from 5 to 50 per cent. The following are the yields obtained from these ingredients:—

Coal.	Gas per 100 Kilos.	Luminous Power of 150 Litres of Gas.	Coke from 100 Kilos.
Scotch cannel	30·4–35·2	18·1–43·4	30–65
Boghead.			
Scotch	29·2–38·8	26·3–62·6	23–62
Australian	39·5–41·5	48·0–53·6	30–36

Of the nitrogen in coal, according to Schilling, 11 to 17 per cent. are given off as ammonia, 57 to 70 per cent. are left in the coke, and the rest is not determined.

Purification of the Gas.—The crude gas evolved in the retorts rises through a wide iron pipe, and enters by way of the bent tube, *B C*, the hydraulic main, *D* (Fig. 91),

Fig. 91.

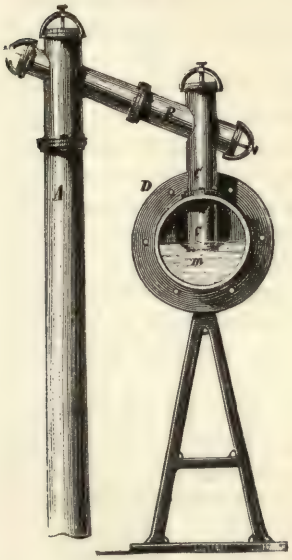
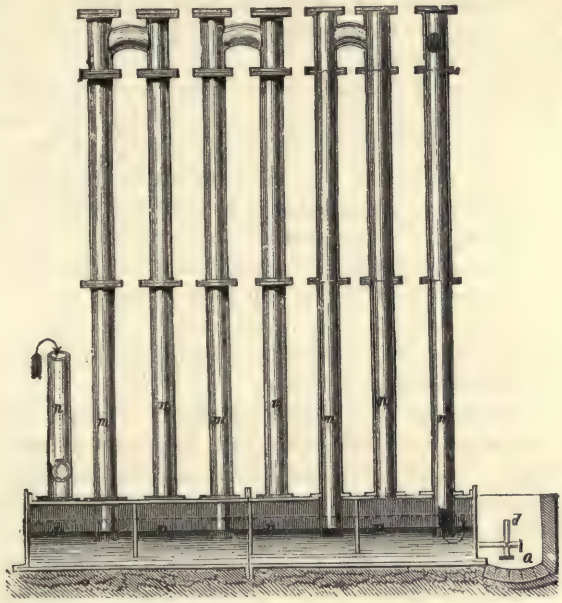


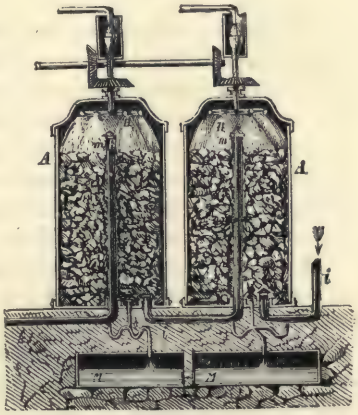
Fig. 92.



which runs over the entire range of furnaces, so as to receive the delivery pipes of all the retorts. Here a portion of the tar and the ammoniacal liquor are condensed, and are run off only so far that the exit-pipes may plunge in to the depth of a few centimetres to prevent the gas from going back into the retorts. An exhauster is introduced into the system, generally after the washing apparatus, to prevent over-pressure.

From the main the gas arrives at the condenser. This generally consists, as shown in section (Fig. 92), of a series of vertical iron pipes, connected above by arched pipes, and standing below on the rectangular cast-iron chest, *P*. The latter is divided into compartments, both in length and breadth. Each compartment has an entrance pipe, *m*, and an exit pipe, *n*. The partitions do not reach quite down to the bottom, so that the liquid which closes the compartments can move freely through the entire chest. In this chest the gas-liquor and the tar are collected. The level of the liquid is regulated by the exit tubes, *d*, through a pipe bent as a siphon. The entrance pipes, which lead downwards, dip a little into the liquid, so that the gas is compelled to pass through.

Fig. 93.



For separating the residue of tar and ammonia the gas is conducted into a scrubber. It consists generally of cylinders, *A* (Fig. 93), 3 or 4 metres in height, filled with fragments of coke, upon which a hollow rotating cross tube constantly sprinkles water. The gas enters through the pipe, *i*, moves upwards among the wet coke, passes down through the tube, *m*, and then enters a second scrubber. At the lowest part of the pipe there is an arrangement for removing the washing water and the tar which collects in the receiver, *M*. Of late the gas is often caused

to pass through sieves which dip into water or over which water flows. For the complete separation of the tar it is desirable that the gas should be compelled to impinge repeatedly on cold surfaces.

Finally, the gas is led into the purifiers in order to remove carbon dioxide (other than that combined with ammonia), sulphuretted hydrogen, carbon disulphide, ammonium cyanide, &c.

The milk-of-lime purifier, introduced by Clegg, has been superseded by the dry-lime purifier (moist calcium hydroxide). In order to give the slacked lime a loose consistence, and to facilitate the passage of the gas to be purified, it is mixed with sawdust, spent tar, &c. Such mixtures are so loose that they may be laid on sieves in layers of 15 to 20 centimetres in thickness without presenting any important resistance, and that, in five layers of 20 centimetres each and spread out in the purifiers, they do not require a pressure of more than 2 or 3 centimetres of water.

According to Veley, the first product formed in this process is calcium hydrosulphate. Gas lime contains, along with unchanged calcium hydroxide and a little calcium cyanide, calcium hydrosulphate in such quantity that gas lime is used by tanners for unhairing hides.

Purifying with Oxide of Iron.—Though copperas was proposed for removing ammonium sulphide from gas, and used as early as 1835, Mallet (1840) was the first to introduce metallic salts, and especially manganous chloride (which was then produced extensively at the chloride of lime works), and also ferrous chloride for the purification of gas on the large scale.

Of much greater importance is the so-called "Laming's mass," introduced by Laming in 1847. As at present used, it consists of ferrous sulphate with lime, to which sawdust is added to render the mass loose. The ferrous sulphate is converted, with the lime, into ferrous oxide and calcium sulphate; the original blackish-green colour of the mixture is changed, by turning over and exposure to the air, to a red, when we have a mixture of ferric hydroxide and gypsum. The mass is used in dry purifiers. Since it has been observed that the lime is of no consequence, iron or manganese oxide, or preferably bog-iron ore, is almost universally used instead of Laming's mass. It is ground fine, mixed with an equal bulk of sawdust, moistened, and used for purifying. Instead of the natural oxide, the residues from the reduction of nitrobenzol by means of iron-filings (in the aniline manufacture) may be used.

According to R. Wagner, the ferric oxide of Laming's mass is first converted by the hydrogen sulphide into iron sesquisulphide, and this compound then passes into ferric oxide, giving up its entire amount of sulphur.

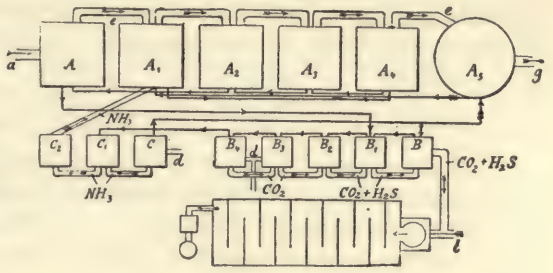
If Laming's mass has been in use for a long time, its efficacy falls off, since the sulphur accumulates up to 40 per cent., and the particles are coated with a glutinous layer, which prevents contact with the gas. From the exhausted mass the sulphur can be recovered by fusion under water at high pressure or by extraction with carbon disulphide; or, after the ammoniacal salts and the iron cyanide (the latter in the form of calcium ferrocyanide) have been removed by lixiviation, the mixture is roasted in kilns, thus producing sulphurous acid for the manufacture of sulphuric acid; and, on the other hand, iron oxide, which may be employed anew in the purification of coal-gas.

For desulphurising coal-gas the mass of Lux has been found satisfactory. It consists of 65 parts ferric hydroxide, 5 parts sodium carbonate, and 30 parts clay, sand, &c. The recent mass takes sulphuretted hydrogen completely up at a velocity of 16 mm. per second. For old, regenerated mass the limit is a velocity of 5 mm. per second. For every 100 cubic metres of gas daily the purifiers must have at least a transverse section of 0·23 square metre.

Ammoniacal Purifying.—According to Claus, the gas when freed as completely as possible from tar passes through six scrubbers (Fig. 94). Almost all the carbon

dioxide is removed in the first, A. In the second it loses the last trace of carbon dioxide, together with the larger portion of hydrogen sulphide. At the upper end of this scrubber, A_1, the ammonia arriving from the stills enters in a continuous current, and, flowing along with the partially purified coal-gas, it passes into the next scrubber, A_2. Here the last trace of hydrogen sulphide is removed, and at the same time a great part of the carbon disulphide contained in the crude gas is eliminated. In the liquid contained in this scrubber the chief part of the ammonia is free, and much of the rest exists as ammonium sulphide. Hence the conditions for removing carbon disulphide from crude gas in this scrubber are favourable. However, in this washer alone there is not presented to the gas a sufficiently large surface moistened with the liquid to effect the maximum possible removal of carbon disulphide. On this account the contents (*e.g.*, coke) of the fourth and fifth scrubbers, which may be named carbon disulphide scrubbers, are kept moistened with a small portion of the liquid from the bottom of the second or third scrubber. From the fifth scrubber the gas passes into A_5. Here the last trace of ammonia is washed out and the gas issues perfectly purified. Over this scrubber is a cistern into which the exhausted liquid from the distillation of ammonia, after it has passed through a refrigerator, is pumped.

Fig. 94.



A quantity of ammonia is stored up in the scrubbers and in the apparatus for the recovery of ammonia, thirty to fifty times larger than the quantity required for taking up the impurities in the largest quantity of crude gas which passes hourly through the scrubbers.

If only an open fire or enclosed steam were used for the distillation of the ammoniacal liquid, after a short time it would become a saturated solution of cyanides and would have to be removed from time to time. Hence the distillation is preferably effected with open steam, for which the waste steam of the engine may be employed. An essential feature in the purification of crude gas with ammonia is the recovery of the cyanides. The liquid contains ammonium ferro-cyanide and sulpho-cyanide.

Whilst Claus distils off the gas-liquor and passes the gaseous ammonia into the scrubbers, F. C. Hills proposed to pump the liquor, freed from carbon dioxide and hydrogen sulphide, direct into the scrubbers. In consequence of successive improvements the two processes almost coincide, as appears from the following report by Watts on Hill's process, as carried out by the South Metropolitan Gas Company. The five scrubbers, A to A_4 (Fig. 94), are 1·3 metre in width and 6 metres in height; the sixth scrubber A_5 is 1·5 metre in diameter and 9 metres high. The crude gas enters the first scrubber at a, passes through the tube e, to the following scrubbers, and escapes, purified, at g. The drawn-out lines show the circulation of the liquid. The towers B are 0·6 metre broad and 4·5 metres high. To two of them steam is conveyed by the pipe d, so that the liquid trickling through the towers (fitted up in the manner of scrubbers) is warmed so much that carbon dioxide and hydrogen sulphide escape whilst the ammonia is distilled off in the tower C. The washing liquid in the five scrubbers contains :—

	A.	A_4.	A_3.	A_2.	A_1.
Ammonia . . .	0·1 ...	1·5 ...	3·5 ...	5·0 ...	4·0
Sulphuretted hydrogen .	— ..	0·1 ...	1·5 ...	2·0 ...	1·5
Ammonium as carbonate	— ...	— ...	— ...	1·0 ...	3·0

The gas-liquor on entering (I.) and leaving (II.) the decomposers *B* contained :—

	I.		II.
Ammonia	4·50	...	4·50
Ammonium as carbonate	4·00	...	1·10
Sulphuretted hydrogen	1·08	...	—

The crude gas contains 0·1 per cent. hydrocyanic acid, which forms this cyanide :—

$$NH_4CN + (NH_4)S_2 = NH_4CNS + (NH_4)_2S;$$

then with carbon disulphide—

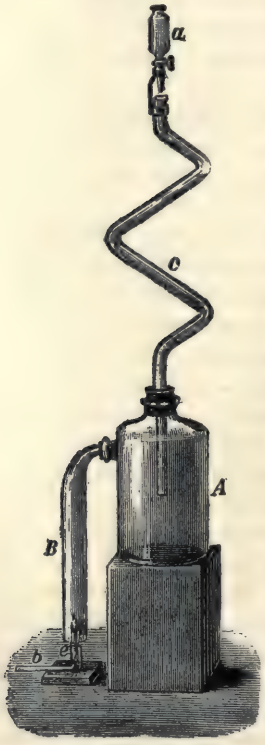
$$(NH_4)_2CS_3 = NH_4CNS + 2H_2S.$$

The finished gas is stored in large bell-gasometers and conveyed for consumption in cast-iron mains tarred. The distribution in houses, &c., is effected through wrought-iron tubes, more rarely leaden ones. [In England lead and composition pipes are unfortunately the most common]. Copper pipes are costly and may become dangerous from the formation of acetylene copper.

Examination.—For checking the process of manufacture the carbon dioxide is determined with the apparatus already described.

The amount of sulphur is determined with the arrangement shown in Fig. 95. The tube *B*, about 25 centimetres long, is secured by a cork to the lateral neck of the bottle *A*, which is also 25 centimetres high. The gas, accurately measured, is conveyed to the glass tube *b* on a small plate, and over its efflux point there is an under glass tube *e*, which slides up and down in a simple holder, so that the whole arrangement represents a glass Bunsen burner. The supply of gas is so arranged that about 20 litres are burnt hourly. Above the repeatedly bent tube *c*, a small dropping vessel *a* is fixed, by means of which during the experiment hydrogen peroxide, free from sulphuric acid and slightly ammoniacal, can be let drop so slowly that every hour 2 c.c. may flow down into the tube *c* to dissolve the last traces of the sulphurous and sulphuric acids formed out of the gases of combustion as they ascend. When about 100 litres of gas have thus been consumed, the tubes *B* and *c* are taken off, rinsed out with a little water, the contents of the bottle *A*, together with the rinsings, are heated to boiling, acidified with hydrochloric acid, and precipitated with barium chloride in the ordinary manner. If the ambient air is not free from sulphuric acid and hydrogen sulphide, the whole arrangement is fixed higher and the interval at *e* is closed in a suitable manner, so that no air can enter except through pumice, moistened with strong potassa lye. One cubic metre of gas should not contain more than 0·3–0·4 grain sulphur. In London 0·57 grain sulphur per cubic metre is permitted ; in Leeds 0·45 grain ; in Cologne 0·23 to 0·39.

Fig. 95.



For determining ammonia in purified gas 200 litres are drawn through 10 c.c. of decinormal hydrochloric acid, and the excess of acid is titrated back.

The complete analysis of gas is effected with the author's apparatus, Fig. 48. Carbon dioxide and oxygen are determined as already described, the tube A is repeatedly rinsed with water, which is drawn off at the cock d ; to remove the last traces of water a few drops of sulphuric acid are allowed to enter A through the funnel t, the mercurial column is lowered in A, and the acid is driven out with mercury through

the tube d. About 0·5 c.c. of strong fuming sulphuric acid is allowed to enter the tube A through the funnel t, and then the sample of gas from the tube M. In about three minutes the sample of gas is forced back into M, the sulphuric acid is let out through the cock d; the funnel t, and the tube A are repeatedly rinsed with water, and the sample is measured in M.

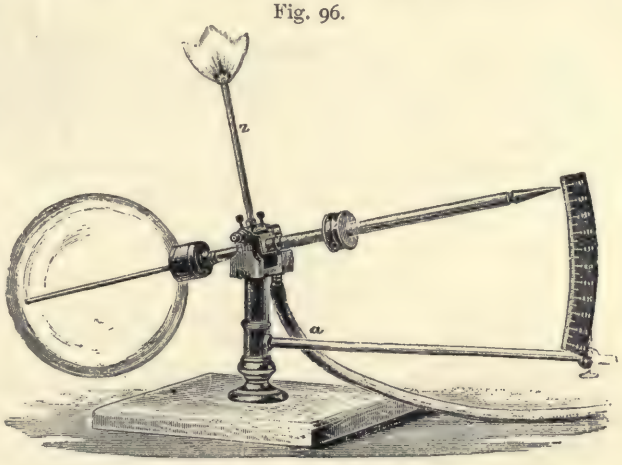
Of this gas freed from CO_2, O, and from heavy hydrocarbons, so much is let escape through the three-way cock that there only remain 50–60 vols. (at ordinary pressure) in the measuring tube M. 60 to 70 vols. oxygen, and about 150 vols. atmospheric air (containing a known amount of oxygen), are allowed to enter, measured; the mixture is ignited by a spark between the platinum wires, the quantity of the residual gas is determined and its proportion of CO_2 and O.

The composition of a sample of gas from the Hannover works was:—

Benzol, C_6H_6	0·69
Propylene, C_3H_6	0·37
Ethylene, C_2H_4	2·11
Methane, CH_4	37·55
H	46·27
CO	11·19
CO_2	0·81
O	trace
N	1·01

For checking the production Lux recommends a continuous determination of the specific gravity. The gas enters through the flexible pipe *a* (Fig. 96), the mercurial joint and the narrow tube into a hollow glass ball, fixed on one arm of a lever, and escapes again at *z*. If the gas becomes heavier, the ball sinks; if lighter, it rises.

Fig. 96.



Wood-gas.—Lebon, as far back as 1799, busied himself with the preparation of illuminating gas from wood. His "thermo-lamp" was quickly abandoned, as its light was not comparable with that of coal-gas. Pettenkofer found in 1849 that if wood is carbonised at a high temperature the gas is more luminous. But, as already stated, even this superior wood-gas has been generally superseded by coal-gas.

Resin-gas.—Colophonium was temporarily used for the production of illuminating gas in several cities in England and the Continent, but it has been given up.

Peat-gas.—Purified peat-gas, according to Reisig, contains—

	I.		II.
Heavy hydrocarbons	9·52	...	13·16
Methan	42·65	...	33·00
Hydrogen	27·50	...	35·18
Carbon monoxide	20·33	...	18·34
CO_2 and H_2S	traces	...	—
Nitrogen	—	...	0·32

Peat-gas will probably never be used on a large scale.

Oil-gas.—If fats, paraffine oil, petroleum residues, &c., are strongly heated they are almost entirely gasified, and form a heavy gas of great illuminating power.

For this purpose the apparatus of J. Pintsch is most generally used. He lets the oil flow slowly down through a U-tube into the iron retort *d* (Figs. 97 and 98), falling

Fig. 97.

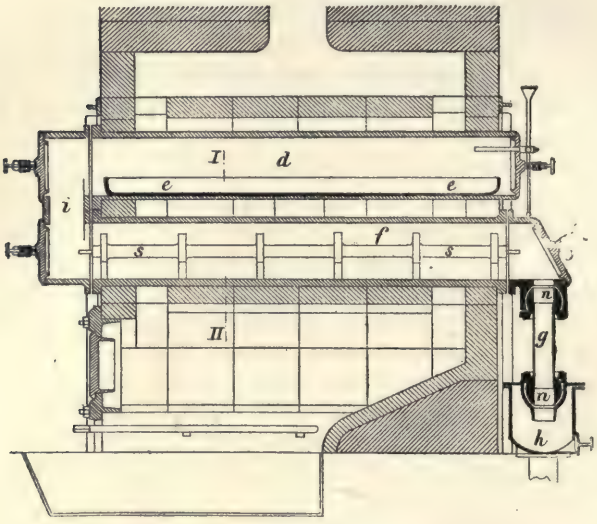


Fig. 98.



Sections I–II.

into the vessel, *e*, where it is completely evaporated, thus facilitating the cleansing of the retorts. The vapours of oil produced here and already partially gasified, pass through the connection, *i*, into the lower cast-iron retort, *f*, in which, for the promotion of gasification there is inserted a piece, *s*, of clay or iron, composed of discs connected by a longitudinal rod. The gas passes now, to deposit tarry vapours, through the pipe, *g*, to the receiver, *h*. The pipe, *g*, is provided with ball joints, so as to follow the expansion of the retort.

Other devices have been proposed by Hirzel, Kühnel, Macadam, and Briehm.

Oil-gas generally requires no particular purification. According to Hilger (1874), paraffine-oil gas has the following composition :—

Heavy hydrocarbons	28·91
Methan	54·92
Hydrogen	5·65
Carbon monoxide	8·94
„ dioxide	0·82

Oil-gas compressed in iron cylinders at a pressure of six to eight atmospheres is of great value for lighting railway carriages. Oil-gas is also suitable for small installations.

Air-gas.—If atmospheric air is saturated with the vapours of volatile hydrocarbons, especially the so-called petroleum ether, it yields an illuminating gas which can only be conveyed to short distances, and cannot bear low temperatures.

The uses of coal-gas are too familiar to need description.*

MINERAL OIL.

According to Herodotus, the mineral oil of the Island of Zante, which he names pissasphaltum, was used for embalming corpses. Plutarch describes a burning pool

* W. J. Cooper has patented a process for improving the quality both of coal-gas and of coke, by adding to the coal before distillation a quantity of lime. The coke as well as the gas is alleged to be, to a great extent, freed from sulphur, so that the purification of the gas is much simplified. Experimental working seems, in some cases, to have given satisfactory results, but we do not know that the process has as yet been formally adopted by any gas company.

of oil near Ecbatana, and Pliny and Dioscorides assert that the petroleum of Agrigentum, in Sicily, was used by the inhabitants for lighting purposes. The mineral oil wells of Baku were known in pre-historical ages, and the same may be said of the springs of Rangoon. The Hannoverian oil-wells were probably found by the first settlers in that district, and their product was used as a lubricant and a medicine 500 years ago. The small spring at Tegernsee has been known since 1430. But mineral oils have first become of importance in commerce since 1879, when the deposits of North America were systematically worked.

Several deposits in Hannover, Holstein, and Alsace have been discovered in Germany. In the Austrian Empire the Galician springs are of importance, and petroleum extends from Austrian Silesia, through Hungary, to Transylvania, as also in Lower Austria, Salzburg, Carinthia, Tyrol, Croatia and Dalmatia. In Roumania there is mineral oil to a considerable extent. In Russia, the springs of Baku appear inexhaustible; in some places fountains of oil shoot up to the height of 30 metres, and flow away unutilised.

There are oil-springs in Burma (Rangoon), in Assam, and in the North-western Provinces of India; in Java and China. In Japan petroleum has been known to occur for 1200 years, but it has only been collected during the last ten years; there are now five refineries at work. Mineral oil has been found in South Australia and New Zealand. The islands of Cuba, Trinidad, and Barbadoes produce petroleum, as do also Mexico, Bolivia, Brazil, and the province Jujuy, in La Plata. North America is especially rich in petroleum. The oil region of Pennsylvania is a narrow belt of country about 100 kilometres in length, between Lake Erie and Pittsburg. There is also an important oil region in Canada.

Concerning the origin of petroleum, the most conflicting views have been advanced by chemists and geologists. Some authorities (Berthelot, Byasson, and Mendeleeff) hold that it has been formed from inorganic materials. Dumas, Rose, and Bunsen assume that mineral oil is derived from the hydrocarbons of the deposits of rock salt. Gregory and Kobell asserted that it was a product of the distillation of coal, of which anthracite is the solid residue. The predominating view at present is that petroleum has been formed by the decomposition of organisms at low temperatures. Well, Kruger, and Windakiewicz, ascribe to it a vegetable origin, whilst Hoefer, Bertels, Müller, and Fraas consider it as a product of the remains of animals.

Mineral oil is rarely obtained by mining. In North America deep borings are the usual source, and the same system is extending in Hannover, Galicia, and at Baku. It is noteworthy that the upper oil region of Pennsylvania, once so productive, has been almost entirely exhausted in ten years, whilst the lower, more southern oil region, which was only opened up in October 1865, now supplies all the petroleum exported from Pennsylvania. The Canadian wells generally run dry in about three years. As the total average yield of a well is 10,540 hectolitres, and as 15 per cent. of the borings in Pennsylvania are unsuccessful, Hoefer calculates the cost of 1 hectolitre of crude oil at the well at 5·8 shillings; after carriage in a pipe line 6½ shillings, or for a barrel of 42 gallons 2·58 dollars, so that in the years 1873 to 1875, and again in the first seven months of 1876, the oil proprietors were working at a decided loss. In Galicia, according to Strippelmann, the cost of 100 kilos. of crude oil is 6·1 shillings.

Hannover and Alsace yield but little oil; Galicia produces yearly 800,000 hectolitres, and the Caucasus 4 millions. The production of crude oil in Pennsylvania rose from 2000 barrels (at 159 litres) in 1859 to ten million barrels in 1874. In 1859 the price was 20 dollars per barrel, and in 1874 it had fallen to 1·29 dollar. The total exportation of the United States in 1886 and 1887 was:—

	1886. hectolitres.	1887. hectolitres.	1887. dollars.
Crude oil	289,320	305,640	5,140,737
Benzene	54,223	46,786	10,439,195
Lighting oil	1,793,750	1,759,108	35,401,044
Lubricating oil and Paraffine	52,111	77,091	3,504,942
Residues	7,556	11,325	141,350

The total value was—

1886 47,016,095 dollars
1887 45,231,988 „

100 litres of crude oil yield on the average 76 litres of lighting oil, 12 litres of gasoline, benzene, &c., 3 litres lubricating oil, and 9 litres of residues.

In Pennsylvania, where most of the wells are exhausted, boring is now not remunerative. The Bradford district, which for years produced more than the total consumption in the world, furnishes now but little; the total production in the remaining districts is estimated at 58,000 barrels daily, while the world's consumption is now daily 70,000 barrels. The consumption of mineral oil has increased not only in America —in 1882, 14,288,905 barrels—but in India, China, Japan, England, France, Spain, and along the Mediterranean. The increase from 1876 to 1882 is estimated at 150 per cent., and the world's consumption for 1876 is taken at 10,000,000 barrels.

The Bradford oil now produced is not nearly so good as it was formerly obtained from Parker's district in Pennsylvania. Of the latter, 100 barrels give 75 barrels of refined oil, whilst 100 of the former yield only 66 barrels. The present so-called refined oil is a product of very light and heavy oils; a complete intermixture is not always practicable. The lighter portions rise to the top and burn first; whilst the heavier oils collect at the bottom, and, if the wick is too thick and too compactly woven, and if the burners are not very carefully cleaned, the light is unsatisfactory. The American refineries are incessantly striving to remedy these evils. But it cannot be denied that oils which have passed the German imperial test are often affected with all these disadvantages. The consumption in Germany for 1882 was 2,001,136 barrels.

Natural Gas.—The gases escaping from the oil wells at (1) Cherrytree, (2) Burns, (3) Leechburg, (4) Harvey, and (5) Bloomfield, have, according to Sadtler and Wurtz, the following composition:—

	1.	2.	3.	4.	5.
Carbon dioxide	2·28	0·34	0·35	0·66	10·11
Carbon monoxide	—	trace	0·26	trace	
Hydrocarbons (C_nH_{2n})	—	—	0·56	—	2·94
Methan (CH_4)	60·27	75·44	89·65	80·11	82·41
Hydrogen	22·50	6·10	4·79	13·50	
Ethylhydrogen (C_2H_6)	6·80	18·12	4·39	5·72	
Propylhydrogen (C_3H_8)	—	trace	trace	trace	
Oxygen	0·83	—	—	—	0·23
Nitrogen	7·32	—	—	—	4·31

According to Fouqué, these American gases belong to the series C_nH_{2n+2}; these are much used for heating steam boilers, for smelting furnaces, &c.

Mineral oil varies in consistence from a thin liquid to a butter-like fat; its colour ranges from that of water to black, and it has sometimes a blue fluorescence; the specific gravity fluctuates between 0·8 and 0·96.

According to Boussingault, the oil from Bechelbronn contains hydrocarbons of the series C_nH_{2n+2}, petrolene corresponds with the formula C_9H_{16}; Blanchet and Sell found in their researches compounds C_nH_{2n} and C_nH_{2n+2}; Warren de la Rue and Müller found C_nH_{2n} and C_nH_{2n+1}. The oil from Sehnde is C_nH_{2n}, but, according to Uelsmann,

it belongs to the series C_nH_{2n+2}. Bussenius obtained from the products boiling between 90° and 140° a trinitropetrol $C_8H_7(NO_2)_3$; according to Eisenstuck, a mixture chiefly of $C_5H_7(NO_2)_3$ and $C_8H_7(NO_2)_3$. According to Le Bell, the mineral oil of the Lower Rhine consists of hydrocarbons of the methan and ethylene series; Joffre detected in the mineral oil of Bruxière de la Grue and Cordesse hydrocarbons absorbed by sulphuric acid belonging to the series C_nH_{2n} and others not absorbed of the series C_nH_{2n+2}, especially of C_8H_{18} to $C_{17}H_{36}$. In the Pennsylvanian oil Warren found C_6H_{14}, Pelouze and Cahours C_5H_{12}, as the most volatile constituent C_5H_{12}, Lefebvre C_4H_{10} and C_3H_8, Ronalds C_3H_8 and C_2H_6.

According to Chandler and Schorlemmer, the oil contains the following hydrocarbons:—

Name ($C_nH_{n_2+2}$).	Formula.	Boiling-point.	Specific Gravity.
Methan	CH_4	Gas	0·559
Ethan	C_2H_6	,,	1·036
Propane	C_3H_8	,,	
Butane	C_4H_{10}	1°	0·600
Pentane	C_5H_{12}	30	0·628

Name.	Formula.	Boiling-point.	Specific Gravity.	Name ($C_nH_{n_2}$).	Formula.	Boiling-point.	Specific Gravity.
Hexane	C_6H_{14}	69°	0·664	Ethylene	C_2H_4	Gas	0·978
Heptane	C_7H_{16}	97·5	0·699	Propylene	C_3H_6	− 18°	
Octane	C_8H_{18}	125	0·703	Butylene	C_4H_8	+ 3	
Nonane	C_9H_{20}	136	0·741	Amylene	C_5H_{10}	35	0·663
Dekane	$C_{10}H_{22}$	158	0·770	Hexylene	C_6H_{12}	69	
Endekane	$C_{11}H_{24}$	182	0·765	Heptylene	C_7H_{14}	95	
Dodekane	$C_{12}H_{26}$	198	0·776	Octylene	C_8H_{16}	104	
Tridekane	$C_{13}H_{28}$	216	0·792	Nonylene	C_9H_{18}	140	
Tetradekane	$C_{14}H_{30}$	238		Dekatylene	$C_{10}H_{20}$	160	
Pentadekane	$C_{15}H_{32}$	258		Endekatylene	$C_{11}H_{22}$	195	0·782
	$C_{18}H_{38}$			Dodekatylene	$C_{12}H_{24}$	216	
	$C_{20}H_{42}$			Dekatritylene	$C_{13}H_{26}$	235	0·791
	$C_{23}H_{48}$			Cetene	$C_{16}H_{32}$	275	
	$C_{25}H_{52}$			?	$C_{20}H_{40}$		
Paraffine	$C_{27}H_{56}$			Cerotene	$C_{27}H_{55}$		
,,	$C_{30}H_{62}$	370		Melene	$C_{30}H_{60}$	375	

Hemilian has furthur obtained from the Pennsylvanian oil a hydrocarbon melting above 300°, petrocen $C_{32}H_{22}$; Röttger separated from the fraction boiling between 55° and 65° a white body $C_5H_{10}SO_3$. If the vapours of mineral oils boiling at low temperatures are passed through ignited tubes, we obtain, according to Prunier, hydrocarbons of the series C_2H_{2n}.

By fractionated distillation of the crude American oils the following average products are obtained:—

	Per cent.	Boiling-point.	Specific Gravity.
Cymogen			
Rhigolen	—	− 18°	0·625
Gasolin	1·5	− 49	0·665
Naphtha	10·0	82–150	0·706–0·742
Benzene	4·0		
Kerosene	55·0	− 167	0·804
Paraffine oil	19·5	300	0·85–088
Residue and loss	10·0		

Other experiments show a very different percentage of products.

Manufacture.—According to Engler, 100 parts of crude oil contain—

	Pennsylvania.	Galicia.	Roumania.	Alsace.
Easily volatile oils	10–20	3–6	4	
Lighting oils	60–75	55–65	60–70	35–40
Residues	5–10	30–40	25–35	55–60

The residues of the refineries at Baku are the most valuable ingredients, on account of their suitability for lubricants. In these establishments Engler saw only the following three forms of boilers :—

(1) Upright wrought-iron boilers, of a cylindrical shape as tall as wide, with a bottom arching upwards, and a common capital leading to the refrigerator. Capacity, 80 to 100 hecto-kilos, if filled from $\frac{3}{4}$ to $\frac{4}{5}$. They are heated with naphtha residues.

(2) The so-called waggon-boiler (Figs. 99 and 100) consists of the chest-shaped

Fig. 99.

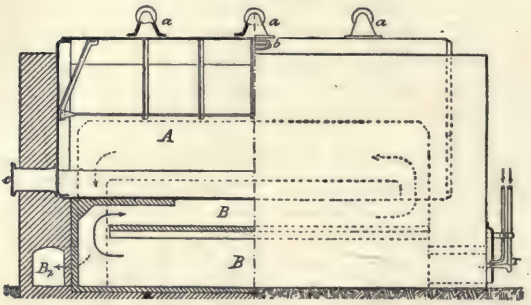
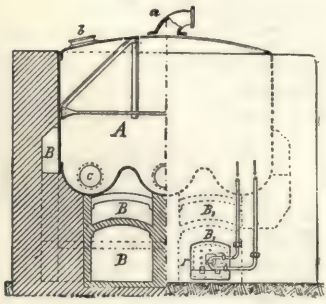


Fig. 100.



boiler of wrought-iron plates rivetted together. The largest size are 7 metres long, 4 metres wide, and 3 metres high from the lowest part of the bottom to the capital. It has a bottom with three undulations, a top slightly arched upwards, and three capitals, *a*, which carry away the vapours to the condenser; *b* is a man-hole; *c* are exit supports for the residues. The inner arrangements of the boiler and the setting with the flues, *B* and B_1, can easily be understood from the figures. From the burner, *r*, of which there are always two side by side, and which open into the arched fire-flues, *B*, B_1, the flame, for the protection of the bottom of the boiler, strikes first through

Fig. 101.

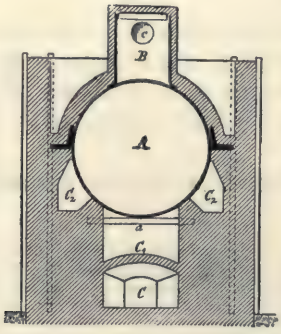
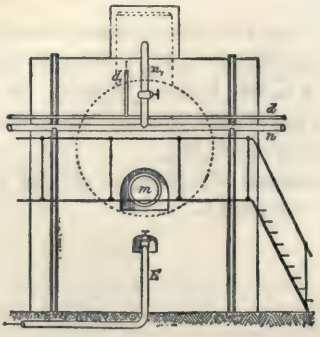


Fig. 102.



fire-proof vaults, turns at the end of the boiler, the bottom of which is here lined with fire-clay tiles, again to the front, ascends and turns at both sides of the boiler, first backwards and then downwards, and escapes into the chimney through the flue, B_2. The distillation is assisted by the introduction of high-pressure steam.

If such a boiler (smaller size) contains 350 hecto-kilos., and is charged with 300 hecto-kilos. of crude oil, $2\frac{1}{2}$ distillations can be effected in twenty-four hours, so that 700 to 800 hecto-kilos. of crude oil are distilled, which corresponds to a daily production of

200 to 250 hecto-kilos. of kerosene. The older setting in which the supporting walls fitted into the depressions of the wave-shaped boiler, so that the three protuberances lay free below and formed three fire-spaces, has been abandoned, as it caused a rapid destruction of the bottom of the boiler.

3. Roller-boiler. Such a boiler is cylindrical, and is shown in Figs. 101 and 102. The materials are wrought-iron plates, 10 mm. in thickness; the length is from 5 to 6 metres, the diameter from 2 to 3 metres; the smaller make, if filled to $\frac{3}{4}$ or $\frac{4}{5}$, hold 170 hecto-kilos. (= 1000 pud.), the largest 270 hecto-kilos. It has not been found practicable to exceed the latter size. The boiler, *A*, lies on bars, *a*, built into the wall, and is further kept in its place by a number of flanges rivetted to its sides. As a provision against boiling over, there is a large dome, *B*, from which the vapours escape through an opening, *c*, into an iron conductor of the same width, by which they are led to the refrigerator. The apparatus for burning residues is introduced at *C*; its flame strikes first through under the vault, passes at the opposite end over the vault into the space C_1, draws forward in the opposite direction directly under the boiler, distributes itself here so as to pass on both sides of the boiler in its original direction through C_2, thus arriving into the common exit flue and into the chimney. If the flames of the residues were let pass underneath the boiler without the protective vault, the burner would have to be placed at least 1·75 metre below the bottom of the boiler, on account of the intense heat. In most refineries a number of distilling boilers are fixed side by side, and behind them runs a common tube with naphtha, from which branch pipes, *n*, pass off for feeding the several boilers, as also a steam-pipe, *d*, with the branch pipe d_1, in order to assist the distillation in each by the introduction of high-pressure steam. *E* is the outflow for the residues placed at the lowest point. The man-hole serves for cleaning out the boiler. As condensers, water refrigerators are uniformly used; they are generally placed behind the distilling boilers, and connected with the capitals by means of iron pipes, either directly or with the interposition of one or more dephlegmators.

As wood and coal are wanting at Baku, the residues boiling at high temperatures are largely used as fuel. For distilling 100 parts of crude oil there are used 3 to 4 parts of these residues, called by the Tartar workman "Massud," and by the Russians "Astatki."

Fig. 103.



The combustion of these residues is effected by pulverising them by means of high-pressure steam; pulverising by means of air does not answer. The air entering is sufficient for combustion, and the temperature of the flames is enough to melt wrought-iron. Fig. 103 shows a burner much used at Baku; it consists of an iron tube, *D*, of the internal diameter of 26 mm., flattened at its front end, so that there only remains a slit of $\frac{1}{2}$ to 1 millimetre, through which the steam can pass. The residues are brought up through the tube, *N*; the thick oil running out at its end is distributed so as to flow down over the steam slit, when it is finely pulverised and then burnt. The arrangement of this burner under a boiler may be seen from Figs. 99 and 100.

The chemical purification of the kerosene obtained on distillation is effected by treatment with sulphuric acid, caustic soda, and water. The apparatus consists of two iron receivers of a cylindrical shape, set above each other like steps. The bottoms are shaped like funnels, with an outflow valve at the bottom, so that the contents of the upper tank can conveniently flow into the lower, and from this, again, into the store tank. The upper receiver, for treating the crude oil with sulphuric acid, is lined with lead.

The "souring" of the oil is effected by an intimate mixture with strong sulphuric acid containing at least 92 per cent. of monohydrate. The quantity used must be the

larger the more rapidly the oil has been distilled. In well-managed works it does not exceed 0·9 per cent. The acid trickles in slowly through a ring of perforated tubes with constant stirring, which is kept up for one and a-half to two hours; the oil becomes heated, and sulphurous acid is given off. It is let settle; the acid which collects below is let off at a special branch-pipe, so that it may be used again, and the kerosene is treated a second time with fresh acid. After this second souring follows a washing process with cold water, which is not especially mixed with the oil, as the separation would be too tedious. After settling for one hour, the oil is run off into the lower tank for treatment with soda-lye. The lye is used first at sp. gr. 1·28 to 1·35, and then a weaker lye is introduced. The quantity of caustic soda used should not exceed 0·3 per cent.

An exactly neutral reaction is aimed at in many refineries. Water is not applied after the soda process. To test kerosene for organic acids (derived from the oil), a sample is shaken up with 2 per cent. of soda-lye at sp. gr. 1·2, let settle, and the clear soda-liquid is acidified. The turbidity arising shows the amount of the existing acid. To ascertain if the treatment with sulphuric acid has been sufficient, a specimen is shaken up with a few drops of soda-lye to form an emulsion, which by reflected light must appear of a pure white without any yellow tinge. The colorimetric test is effected with Stammer's colorimeter. A good burning oil is colourless and clear as water.

The photometric test is executed with Bunsen's photometer with the mirror comparison, the German normal candle being used as a standard. The distillation trial is carried out with a Glinsky dephlegmater, filling the boiling flask each time with 250 cc. of the oil, and taking two hours for the distillation working more slowly towards the end. The flashing-point is determined with Abel's apparatus. Hitherto the limit in Russia has been 28° to 30°, but the manufacturers have resolved on a limit of 25°.

The yield of the various products of the distillation differs according to the manner of working. The more benzene and heavy oils are taken along with the true burning oils—boiling between 150° and 290°—the higher is the yield of the latter and the lower its quality. From numerous reports the following values may be taken :—

Benzene with gasoline . . .	5– 7 per cent.
Kerosene I. (burning oil) . . .	27–33 „
Kerosene II. (solar oil) . . .	5– 8 „
Residues	50–60 „

In general, 3½ parts crude oil are used to obtain 1 part of kerosene. The quicker the distillation the more abundant, but the poorer, is the product. At Nobel's refinery the yield of kerosene of 32° flashing-point is 27 per cent.; of 50°, 23 per cent. The specific gravities for benzene are 0·754, for gasoline 0·787, for kerosene 0·820–0·822.

The cost of production for 1 hecto-kilo. (= 100 kilos.) burning oil (kerosene) are—

	Shillings.
3½ hecto-kilos. crude naphtha	1·78
Sulphuric acid	0·15
Caustic soda	0·11
Wages	0·06
Management	0·07
Boiler repairs	0·18
Sinking fund, 15 per cent.	0·24
	2·59

Besides the kerosene there is 50 per cent. (1·7 hecto-kilos.) of residues, and 26 per cent. of residues are used in heating the works.

The residues are especially adapted for the production of lubricating oils. These oils are valuable from their viscosity, their resistance to cold, and their non-liability to spontaneous combustion.

Not merely kerosene, but the lighter products, gasoline, naphtha, and ligroine are often burnt in lamps of special construction. The residues, as well as the crude oil, may be heated in retorts for the production of gas. Compressed cymogen, boiling at 0°, is used in the production of artificial ice; Rhigolene Rhyolan, boiling at 18°, serves as an anæsthetic; naphtha (petroleum-ether, or canadol) for extracting fatty oils; benzene for colours, varnishes, and for taking out spots, and the heavier oils (vulcanol, vaseline, and valvoline) serve as lubricants.

THE PARAFFINE AND SOLAR OIL INDUSTRY.

Paraffine was first discovered in 1830 by Reichenbach in beech-wood tar, and received its name from its disinclination to combine with other bodies. It was subsequently obtained by the dry distillation of peat, lignite, Boghead coal, oil-shales, &c. It occurs also in nature ready formed in mineral oil, which may contain from 6 to 40 per cent.; in ozokerite (mineral wax) and in bitumen, or asphalte. The American mineral oils contain little paraffine, but those of India (Rangoon tar) and of Java contain large proportions. Warren de la Rue in 1854 obtained a patent for the extraction of paraffine and hydrocarbons from mineral oils. The paraffine obtained as a residue in refining the Pennsylvanian mineral oil is now met with in commerce and extensively used under the name vaseline. It is employed in ointments, pomades, and for protecting metal articles from oxidation. Very similar preparations are sold as "ozokerine" and "Virginia."

Paraffine has been obtained for ten years from ozokerite. This mineral is found in Galicia, on the northern slope of the Carpathians, in Roumania, Bulgaria, and various places in Austria and Germany. It occurs also in Texas, Arizona, and Utah.

Paraffine is obtained in Scotland from asphalt. The bitumen of Trinidad, Cuba, Canada, &c., forms a source for the preparation of paraffine and liquid fuels.

The manufacture of paraffine by the dry distillation of peat, lignite, oil-shales, &c., resolves itself into two branches—the preparation of tar, and the extraction from it of photogen, solar oil and paraffine. The former process is difficult and important; it is now generally performed in upright retorts, preferably of fire-clay.

Preparation of the Tar.—1. This operation is one of the most important and difficult parts of the industry, and during the last fifty years many enterprises undertaken for the application of fossil fuel to the preparation of illuminating materials have failed solely on account of the imperfect preparation of the tar. The making of the tar is carried on in retorts or in peculiarly constructed ovens, the distillation being in many cases assisted by the application of superheated steam. The principle of the construction of the tar-oven is very simple, being that of a portion of fuel burning in the lower part of the oven, a layer, more or less thick, of superincumbent fuel is submitted to a slow carbonisation, resulting in the production of tar, which flows downwards, while the gaseous products are lost. In order to prevent its violent combustion, the fuel is covered with a layer of clay. But as experience has shown that this mode of distillation is not well suited for the production of tar intended to yield paraffine and the oils, it is not generally in practice on the large scale, although it has the advantage of being a continuous and uninterrupted process. According to report, an oven constructed by L. Unger, the manager of a paraffine works at Dollnitz, near Halle, yields suitable products, while a saving is effected in labour as well as in the quantity of fuel required for the distillation.

Horizontal retorts are frequently used for the preparation of tar, but experience has taught that if in the construction of the furnaces containing the retorts the arrangement is similar to that of a gasworks where four to eight retorts are worked in one furnace, no satisfactory results can be obtained, one of the reasons being that

the principles of gas- and of tar-making are entirely opposed. It appears to be necessary to construct a furnace for every retort, and that the furnace should be of such dimensions as to be suited to hold a retort 10 feet long, 30 inches wide, and 15 inches high, forming in section a shallow oval. More recently there have been built in Bohemia and elsewhere brickwork retorts, shaped somewhat like a baker's oven. These seem to answer well, but are difficult to repair, although of small first cost. Vohl observed that a quantity of 20 to 25 per cent. of water present in the fossil material very greatly assists the formation and increases the yield of tar, owing to the superheated steam formed from the water during the distillation carrying off the vapours of the tar rapidly from the hot retort. This has given rise to the construction of Lavender's tar-producing apparatus, the principle of which is the same as that of Violetti's wood-charring apparatus used for the preparation of the charcoal in gunpowder manufacture. Lavender's apparatus consists of an iron cylinder provided with holes at the bottom for the purpose of admitting superheated steam, while to the top of the cylinder a tube is fitted for carrying off the products of the distillation. It would appear that L. Ramdohr's method of preparing tar from brown-coal by means of steam yields a tar which contains 22 to 24 per cent. of paraffine, and 36 to 38 per cent. of oil.

Condensation of the Vapours of the Tar.—The condensation of the products of the dry distillation is one of the most important operations, and greatly influences the yield of tar. Vohl has lately proved that even when the construction of the retorts is not of the best, an average yield of tar may be obtained by attention to the condensation of the vapours. The complete condensation of the vapours of the tar is one of the most difficult problems the paraffine and mineral oil manufacturer has to deal with, while the means usually adopted for condensation, such as large condensing surfaces, injection of cold water, and the like, have proved ineffectual. It has often been attempted to condense the vapours of tar in the same manner as those of alcohol, but there exist essential differences between the distillation of fluids and dry distillation. In the former case the vapours soon expel all the air completely from the still and from the condenser, and provided, therefore, that—in reference to the size of the still and bulk of the boiling liquid—the latter be large and cool enough, every particle of vapour must come into contact with the condensing surfaces. In the process of dry distillation the case is entirely different, because with the vapours, say of tar, permanent gases are always generated. On coming into contact with the condensing surfaces, a portion of the vapours is liquefied, leaving a layer of gas as a coating, as it were, on the condensing surface. The gas being a bad conductor of heat, prevents to such an extent the further action of the condensing apparatus, that a large proportion of the vapours is carried on and may be altogether lost. A sufficient condensation of the vapours of tar can be obtained only by bringing all the particles of matter which are carried off from the retorts into contact with the condensing surface, which need neither be very large nor exceedingly cold, because the latent heat of the vapours of tar is small, and consequently a moderately low temperature will be sufficient to condense these vapours to the liquid state. The mixture of gases and vapours may be compared to an emulsion, such as milk, and as the particles of butter may be separated from milk by churning, so the separation of the vapours of tar from the gases can be greatly assisted by the use of exhausters acting in the manner of blowing fans. It is of the utmost importance in condensing the vapours of tar that the molecules of the vapours be kept in continuous motion, and thus made to touch the sides of the condenser. The condenser should not be constructed so that the vapours and gases can flow uninterruptedly in one and the same direction. The temperature at which the distillation is conducted greatly influences the yield of tar, and consequently of the paraffine and oil. As regards the influence of the shape of the retorts and mode of distillation, H. Vohl made the undermentioned comparative researches by distilling French and Scotch peat in

horizontal retorts (No. I.), in vertical retorts (No. II.), and in ovens somewhat like coke-ovens (No. III.).

100 parts of peat yield of tar,—

	I.	II.	III.
French peat . . .	5·59	4·67	2·69
Scotch peat . . .	9·08	6·39	4·16

The sp. gr. of the tar from the different kinds of apparatus was as follows:—

	I.	II.	III.
French peat . . .	0·920	0·970	1·006
Scotch peat . . .	0·935	0·970	1·037

It appears from these results that horizontal retorts yield the largest, and ovens the smallest, quantity of tar; moreover, the duration of the operation of distilling is shortest in horizontal retorts, which also yield less gas, while in the ovens both tar and coke are burnt away to a considerable extent by the too great supply of oxygen.

Properties of Tar.—The tar obtained from the retorts in distilling peat, brown-coal, lignite, bituminous shales, Boghead coal, &c., at as low a temperature as possible, and hardly higher than dull red-heat even towards the end of the operation, exhibits a coffee-brown colour, generally an alkaline, but in some instances an acid, reaction, and possesses the very penetrating odour characteristic of tar. By exposure to air the colour of the tar becomes deeper, and sometimes even brownish-black. This tar often semi-solidifies at a temperature of 9° to 6°, owing to the paraffine it contains. The sp. gr. varies from 0·85 to 0·93, and consequently the tar floats on water. The so-called steam-tar, obtainedby the aid of superheated steam from brown-coal (according to Ramdohr's plan, 1869) always has an acid reaction, and is completely saponified by alkalies; this tar becomes solid at a temperature of 55° to 60°, and can therefore be preserved in solid blocks in summer time. Its sp. gr. is 0·875.

As regards the quantity of tar obtained from 100 parts of raw material, the following results are most general:—

		Tar.	Sp. Gr.	Crude Paraffine. per cent.
Foliated bituminous shale,	Siebengebirge	20·00	0·880	0·750
„ „ „	Hesse	25·00	0·880	1·000
Brown-coal,	Prussian Saxony	7·00	0·910	0·500
„	„	10·00	0·920	0·750
„	„	6·00	0·915	0·500
„	„	5·00	0·910	0·250
„	Bohemia	11·00	0·860	
„	Westerwald	5·50	0·910	
„	„	3·50	0·910	
„	Nassau	4·00	0·910	
„	„	3·00	0·910	
„	Frankfort	9·00	0·890	
Lignite,	Silesia	3·00	0·890	0·250
Shale,	Vendée	14·00	0·870	1·000
„	Westphalia	5·00	0·920	0·050
Schist,	Würtemburg	9·63	0·975	0·124
Peat,	Neumark	5·00	0·910	0·330
„	Hannover	9·00	0·920	0·330
„	Erzgebirge	5·70	0·902	0·350
„	„	5·30	0·905	0·400
„	Russia	5·86		
„	„	7·00		
Boghead coal,	Scotland	33·00	0·860	1–1·4
Cannel coal,	„	—	—	1–1·3
Peltonian coal	„	—	—	1·000
Coarse coal,	„	9·00	0·910	1–1·25

Mode of Operating with the Tar.—The first thing to be done with the crude tar is to separate the water, which is effected by pumping the tar into the dehydrating

apparatus. These apparatus consist of tanks of boiler-plate, placed within a larger tank, so that a space of 10 centimetres intervenes, into which water is poured and maintained by means of steam at a temperature of 60° to 80° for ten hours. After this time the ammoniacal water and other impurities, together about one-third of the bulk of the crude tar, have become separated, while the small quantity of water still adhering to the tar is of no consequence in the further operations. The tar is decanted by opening a stop-cock or valve placed near the top of the tank, and the ammoniacal water is removed by opening a stop-cock at the bottom.

Specifically light tars are of course readily separated from the water, while heavy tars are more difficult to deal with. If to the ammoniacal water of such tars salts are added—for instance, common salt, Glauber salt, chloride of calcium, and the like—the specific gravity of the water is increased, and the heavy tar more readily separated; but, according to Dullo, these means are either too expensive or do not quite answer the purpose. The complete separation of the tar from the water is of the greatest importance, because in the subsequent distillation the presence of water may cause the tar to boil over and give rise to serious accidents by coming in contact with the fire under the stills.

Distillation of the Tar.—This operation is usually carried on in cast-iron stills large enough to hold 20 cwt. of tar. In order to prevent the flame impinging on the bottom of the still, it is protected by a fire-brick arch. The still is usually built in two separate parts, which are joined with a flange and bolts, so that if the lower part is burnt out, only that requires to be renewed.

The capitals of these stills are rather flat and the spout very wide. The vapours of the various oils have a high density and low latent heat, so that these vapours have a tendency to condense readily and flow back into the still; therefore the capital is covered with sand or ash, being bad conductors of heat. When the tar is thoroughly dehydrated, the distillation proceeds quietly and without ebullition; but if any water be mixed with or adheres to the tar, the liquid in the still boils violently and is very apt to boil over. At below 100° the tar loses the very volatile sulphide of ammonium and the pyrrhol bases, while gases are evolved which ought to be allowed to escape by a safety-valve. The true distillation begins at 100°, yielding at first a distillate consisting of very strong ammoniacal liquor and some light oils. The boiling-point of the tar is not constant, the oil coming over uninterruptedly when the temperature has risen to above 200°; then the boiling-point becomes somewhat constant, while with the oil some water comes over, due to the chemically combined water of the carbolic acid being set free. The distillation then again becomes somewhat interrupted, and can be maintained only by stronger firing of the retort. The oils now distilling over become solid on cooling, owing to the large proportion of paraffine they contain. The distillation is continued to dryness, the asphalt left in the still being removed after about four or five operations, and for this purpose the still is somewhat cooled, and the molten asphalt run off by a tap at the bottom of the still. If the distillation is carried to dryness, some water finally distils over, due to the decomposition of the organic matter. A still of 500 litres capacity can be distilled off in twelve to fourteen hours, if the operation is pushed so far as to decompose the asphalt, leaving only a carbonaceous residue; but if the asphalt is to be collected, the distillation must be stopped after eight to ten hours. The still is separated from the condensing apparatus by a massive wall, through which the spout of the capital is passed into the leaden worm, serving as a condenser, and kept cool by being placed in a wooden tank filled with cold water. But as soon as the paraffine magma begins to come over the water is allowed to become warm, in order to prevent the paraffine solidifying in the worm. The gases which are evolved towards the end of the distillation are carried off by a pipe communicating with the chimney.

Treatment of the Products of Distillation.—The mixed products of raw oils

obtained by the distillation are poured into a large cast-iron cylinder and mixed with a solution of caustic soda so as to cause the latter to act upon, and intimately combine with, the acid substances (homologues of carbolic acid)—simply termed creosote in the works—and pyroligneous acid, which impart an offensive odour and dark colour to the oils. When the mixture of the oils and caustic soda solution has been effected, the fluid is run into an iron tank and allowed to settle; the creosote-soda is then removed, and the oil washed with water to eliminate any adhering alkali. The crude oil is next similarly treated with sulphuric acid for the purpose of removing basic substances, which impart odour and colour. The quantity of acid to be used and the duration of its action, aided sometimes by heat, depend upon the nature of the crude oil—5 per cent. of acid of 1·70 sp. gr. and five minutes' action are sometimes sufficient, while in other cases 25 per cent. of acid will be required, and three hours' contact with the oil. The action of the sulphuric acid should be carefully watched, as it may injure the quality of the oil by decomposing some of the lighter hydrocarbons, whereby sulphurous acid is given off. The mixture of acid and oil is allowed to settle; the former is run off, and the latter washed first with water, then with very dilute soda-lye, and is finally poured into the rectifying stills. The solution of creosote-soda is neutralised with the sulphuric acid from the preceding operation, the result being that crude carbolic acid is obtained, which is used for various purposes; such as impregnating wooden railway sleepers, as a disinfecting material, or for preparing certain tar-colours. More recently the creosote-soda has been used for gas manufacture, leaving a coke containing soda, the soda being abstracted by lixiviation with water.

Rectification of the Crude Oils.—This operation is conducted precisely as the distillation of the tar. The oils are separated according to their greater or less volatility and specific gravity, or are kept mixed, as paraffine oil, at a sp. gr. of 0·833, and sent as such to the market. When the oil which comes over begins to solidify on cooling or exhibits a sp. gr. of 0·88 to 0·9, it is separately collected and placed in a cool situation for the purpose of crystallising the paraffine. The vessels in which the paraffine magma is placed for the purpose of solidifying are rectangular iron tanks, fitted with a tap, or are conical, sugar-loaf-shaped vessels, made of iron or wood, and from 1·6 to 2 metres high, and 1 metre wide at the top, being provided with a tap for the purpose of removing the oily matter which has not solidified after the lapse of about two to four weeks. This thick oil is next cooled to far below the freezing-point of water, in order to obtain more paraffine and other hydrocarbons mixed with it. Any still non-solidified matter is, when it has a low specific gravity, again refined by distillation, and will yield paraffine oil; but if its sp. gr. is high—say from 0·925 to 0·940—it is used as a lubricating oil, known abroad as Belgian waggon grease.

Refining the Crude Paraffine.—The crude paraffine is in England sold to the refiners, who are also paraffine-candle makers; but on the Continent every manufacturer of crude paraffine refines his products and converts it into candles. The crude paraffine, so-called paraffine butter, is treated in various ways: some manufacturers crystallise it by the aid of cold, and press it for the purpose of removing any oil; others, again, first treat the crude material with caustic alkali-lye, next with sulphuric acid, and then again distil it or leave it to crystallise. The caustic soda-lye removes from the paraffine all the acid substances and other impurities it may contain. The partly purified paraffine is now treated with 6 to 10 per cent. of sulphuric acid, whereby alkaline and resinous matters are removed. The loss in bulk of the crude material by these operations amounts to about 5 per cent. The purified paraffine is next allowed to remain in a very cool place for some three or four weeks, after which the nearly solid mass is filtered, then submitted to the action of centrifugal machines, and finally strongly pressed. The oil which is separated from the paraffine is again distilled, yielding paraffine oil and paraffine butter. The solid paraffine is molten, cast into blocks, and these

submitted to very powerful hydraulic pressure. The pressed cake is next treated at 180° with 10 per cent. of sulphuric acid for two hours, then washed with hot water, again cast into blocks, again pressed, and then washed with a solution of caustic soda. Instead of treating the paraffine with active agents, it has been proposed to use neutral solvents for the removal of the oily materials; for this purpose, benzol, light tar oils, benzolene, and sulphide of carbon, have been employed in the following manner:—The crude paraffine is first hot-pressed, and the pressed mass fused with 5 to 6 per cent. of the solvent; having been again cast into blocks, these are pressed, and the operation repeated if necessary. The paraffine having thus been made quite white and pure, is again fused and treated with high-pressure steam, forced into the molten mass for the purpose of volatilising the last traces of the solvents. The sulphide of carbon, first employed by Alcan (1858) for refining paraffine, is used in the following manner:—The paraffine is melted at the lowest possible temperature, then well mixed with 10 to 15 per cent. of sulphide of carbon, after which the cooled and solidified mass is strongly pressed, the expressed fluid being submitted to distillation for the purpose of recovering the sulphide of carbon. The paraffine is next fused and kept in liquid state for some time for the purpose of eliminating the adhering sulphide of carbon.

Hubner's Method of Preparing Paraffine.—Instead of following the preceding method with the crude tar, Hubner treats it first with sulphuric acid, and next distils the tar, separated from the acid, over quicklime. The crude paraffine obtained is pressed, and then further refined by treating it with colourless brown-coal tar oil. The advantages of this method—by which *one* distillation is saved—are:

α. A larger yield of paraffine.

β. A material of better quality and greater hardness than by the usual method.

With the paraffine the so-called paraffine oils are obtained; but this industry has been greatly crippled by the extensive importation of paraffine oils (really petroleum oils) from America, so that the aim of the paraffine makers is to increase the yield of paraffine. By Hubner's method of distillation over quicklime, 40 to 50 per cent. of impurities (chiefly empyreumatic resins and creosote) are removed, which by the old process are only got rid of at greater expense by the use of caustic soda.

Yield of Paraffine.—As regards the yield of paraffine, paraffine oil, and lubricating oil, from the various kinds of raw materials, we quote the following particulars. At the Bernuthsfeld works, near Aurich, the excellent peat yields 6 to 8 per cent. of tar; 20 per cent. of paraffine oil, of sp. gr. = 0·830; and 0·75 per cent. of paraffine. H. Vohl obtained from 100 parts of peat-tar from the peat of undermentioned localities:—

	Paraffine Oil. Sp. gr. 0·820.	Lubricating Oil. Sp. gr. 0·860.	Paraffine.
Celle (Hannover)	34·60	36·00	8·01
Coburg	20·62	26·57	3·12
Damme (Westphalia)	19·45	19·54	3·31
Zurich (Switzerland)	14·40	8·66	0·42
Russia	20·39	20·39	3·36
Westphalia	11·00	19·48	2·25

Brown-Coal.—In the works situated in the Weissenfels brown-coal mineral district, 275 to 300 lbs. of the mineral yields 35 to 50 lbs. of tar. 100 lbs. of this tar yield 8 to 10 lbs. of hard paraffine suited for candle-making, and further 8 to 10 lb. of soft paraffine for use in stearine-candle making, as well as 43 lbs. of paraffine oil. Hubner's works at Rehmsdorf, near Zeitz, yield annually from 360,000 cwts. of brown-coal, about 40,000 cwts. of tar, yielding 18,000 cwts. of crude oil, 4000 cwts. of refined paraffine oil, and 6000 cwts. of paraffine.

100 parts of retort-tar (in contradistinction to steam-tar) from brown-coal yield :—

Brown Coal from—	Paraffine Oil. Sp. gr. 0·820.	Lubricating Oil. Sp. gr. 0·860.	Paraffine.	Analysed by
Ascherleben, Prussia	33·50	40·00	3·3	Vohl.
Frankenhausen „	33·41	40·06	6·7	
Münden „	17·50	26·21	5·0	
Oldisleben „	17·72	26·60	4·4	
Cassel „	16·42	27·14	4·2	
Der Rhön, Bavaria	10·62	19·37	1·2	
Tilleda, Prussia	16·66	18·05	4·4	
Stöckheim, near Düren, Prussia	17·50	26·63	3·2	
Bensberg, near Cologne „	16·36	19·53	3·4	
Tscheitch, Austro-Hungary	9·04	28·86	3·2	C. Müller.
Eger „	9·14	54·00	5·2	
Herwitz „	22·00	48·32	5·2	
Schöbritz „	21·68	46·33	4·3	

Ramdohr obtained (1869) from steam-tar from brown-coal on an average—

22 to 24 per cent. paraffine { 15 per cent. fusing at 56° to 58° / 7 to 9 „ „ 38° to 47° } and
36 to 38 per cent. of oil.

With careful management steam-tar may yield from 28 to 30 per cent. paraffine.

The quotations of the yield from cannel and Boghead coals vary very much. 100 parts of tar from bituminous shale were found to yield :—

	Mineral Oil.	Lubricating Oil.	Paraffine.
English bituminous shale	24·28	40·00	0·12
Bituminous shale from Romerickberg, Prussia	25·68	43·00	0·11
„ „ Westphalia „	27·50	13·67	1·11
„ „ Oedingen on the Rhine „	18·33	38·33	5.00

According to Müller (1867), 100 parts of Galician mineral wax (ozokerite) yield 24 per cent. of paraffine and 40 per cent. of oil.

Paraffine when purified is a white, waxy, tasteless, and inodorous mass, slightly greasy to the touch, harder than tallow, but softer than wax. Its sp. gr. varies from 0·869 to 0·943, and its specific heat = 0·683. If heated for days with access of air it takes up oxygen and turns brownish. Its properties vary according to its origin. Paraffine from the Boghead coal melts at 45°, and is either crystalline or granular ; but it has been known to melt at 80°. Paraffine from Rangoon tar melts at 61°, that from peat at 47°, that from ozokerite at 56° to 82°. Paraffine seems to be a mixture of hydrocarbons homologous with methan (of the formula C_nH_{2n+2}), and especially of members of this series containing more than 16 atoms of C. The softer paraffines have the formulæ $C_{18}H_{40}$, and $C_{20}H_{42}$; whilst the harder varieties are $C_{21}H_{44}$ and $C_{22}H_{46}$. Grotowsky found in paraffine from Saxon lignite 3·4 per cent. of oxygen, and gave it the formula $C_{32}H_{33}O$.

Paraffine is insoluble in water, but soluble in alcohol, ether, oil of turpentine, olive oil, benzol, chloroform, and carbon disulphide. Acids and alkalies do not attack paraffine at common temperatures ; neither does chlorine, but if it is allowed to act for some time upon melted paraffine, hydrochloric acid is evolved, and chlorised products are formed. If heated with bromine it forms hydrobromic acid in abundance, and with sulphur sulphuretted hydrogen.*

Paraffine can be melted along with wax, stearine, and palmitine in any proportion.

The main application of paraffine is, of course, in the manufacture of candles. Its minor uses are for saturating matches, greasing leather, preparing wax-papers, polishing glazed-paper, &c.

* The latter reaction has been proposed as a means of obtaining sulphuretted hydrogen absolutely free from arsenic, for use—*e.g.*, in toxicological cases.

Along with paraffine, Reichenbach discovered in tar eupion a very light mobile fluid, which burns with a luminous flame. Its boiling-point varied from 47° to 169° so that it was doubtless a mixture.

Solar Oil.—Tar-oil can be resolved by further rectification into paraffine and into oily liquids, which, after the acid and the heavy constituents are removed, occur in commerce as a mixture under the names photogene, mineral oil, solar oil, paraffine oil (which in England denotes the lamp oil obtained from the Boghead mineral). These oils are very similar to petroleum oils and consist only of carbon and hydrogen. When thoroughly purified they are colourless and have only a slight smell.

The mineral oils are thus distinguished—photogene is a mixture of liquid hydrocarbons of the ethase series (C_nH_{2n+2}) especially of Leptase, C_7H_{16} and benzyl-hydride, $C_{15}H_{32}$. It is a clear, very mobile liquid of sp. gr. 0·80 to 0·81; the earlier light photogenes of 0·78 sp. gr. contain chiefly essences of sp. gr. 0·720, boiling below 60°. They have hence been long ago proscribed as dangerous. The low-boiling oils from lignite tar and mineral oil are sold by the names benzene (benzolene, naphtha, ligroine) and are used for taking out fat and oil stains, for removing the grease of wool, as a substitute for oil of turpentine, for enriching gas, &c. The solar oil, which is being substituted as an illuminant for the photogenes and the fatty oils of the past, is a clear oil, colourless and slightly yellowish, of sp. gr. 0·825 to 0·830. The boiling-point is on the mean 178°. At 10° no solid paraffine should separate out. Its flashing point is above 100°. On fractionation no products having a flashing point below 70° should separate out.

Along with solar oil follows the pyrogene of Breitenlohner, obtained from the residuary crude oils, having a sp. gr. of 0·895 to 0·945, which accumulate in the tar-works. Pyrogene is a light wine-yellow oil of sp. gr. 0·825 to 0·845.

Lubricating oil, known also as "vulcanol," is a thick oil of sp. gr. 0·845 to 0·860, and at low temperatures deposits abundance of fine crystals of paraffine. It is formed in great quantities in the petroleum refineries and in the paraffine and solar oil works. The vulcanol imported from America is not a distilled product, but a heavy mineral oil decolorised by means of bone-black. Sometimes it is mixed with a few per cents. of animal or vegetable fats.

The manufacture of mineral oil is developed simultaneously with that of paraffine. Solar oil gives, in suitable lamps, a light equal in intensity to that of kerosene. It has, however, an unpleasant smell and is apt to smoke.*

PRODUCTION OF LIGHT.

If solids are heated they become feebly luminous in the dark about 400°; at 600° they are red-hot, at 900°–1000° white hot, whilst gases even at 1500°–2000° do not become luminous. The luminosity of flame is therefore not the ignition of the products of combustion. If the gases arriving at combustion are more quickly mixed, the flame becomes shorter, since the process is effected more rapidly, and at the same time hotter, since less cold air is mixed with the products of combustion. In the same manner, the flame becomes shorter and hotter if the gases are heated prior to combustion. As the ascending products of combustion retain for a short time nearly the temperature of the flame, the reverse behaviour would occur if the gases were self-luminous. The light of the flame ceases at a sharply marked upper boundary, and evidently coincides with the completion of the chemical action. This action consequently, and not the ignition of the products of burning, must be the cause of the light.

* It must seem strange that the author should have made no mention of the merits of the late James Young in connection with the paraffine industry. The only mention of his name is in a note giving the statistics of Young's Mineral Oil Company.—[EDITOR.]

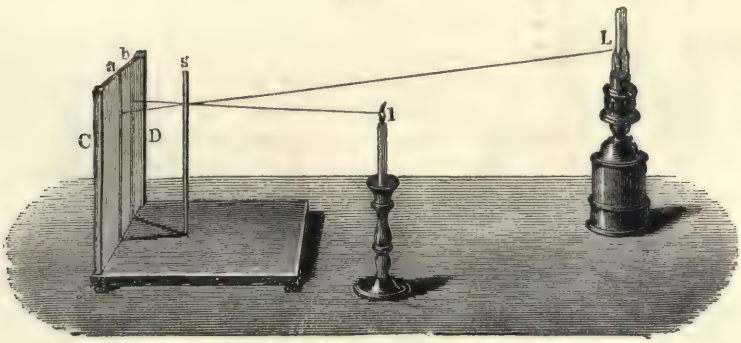
In the flame of a candle we may distinguish four layers. The dark nucleus is formed by the gasification of the fuel (tallow, paraffine, &c.) rising up in the wick, which may be kindled at the orifice of a fine glass tube cautiously inserted into the flame. The rush of air is directed towards the axis of the flame, whence the blue portion has a lower temperature. In the luminous layer the oxygen of the air is only in part sufficient for combustion, whilst in the non-luminous veil externally the products of the imperfect oxidation burn in an excess of air.

In opposition to the well-known theory of Davy that the luminosity of a flame is due to particles of carbon ignited to whiteness by the combustion of the hydrogen, Frankland and Tyndall maintain that the luminosity is due, not to the separation of solid carbon, but to the presence of dense vapours of the higher hydrocarbons.

PHOTOMETRY.

Attempts at measuring the luminosity of a flame were made as early as 1700. Lambert (1760) utilised the circumstance that an object illuminated by two flames throws two shadows of unequal depth if the action of both flames upon the screen receiving the shadows is unequal. Let C D (Fig. 104) be a white screen, before which

Fig. 104.



stands at some distance a thin round rod, blackened with soot, s, and let l be the one and L the other source of light. The two lights are placed so that the two shadows of the rod, a and b, do not coincide, but fall upon the screen, C D, at no great distance from each other. The stronger light is then pushed so far from the screen, C D, that the shadows are equally dark—*i.e.*, the shadow, b, is as strongly illuminated by the light, L, as is the shadow, a, by the light, l. The process is not adapted for accurate measurements, but it is simple and easy, and may even now serve for the purposes of daily life.

Bunsen's photometer is chiefly used for measuring different sources of light. It consists of a paper screen stretched in a frame, and in the middle is a spot made translucent with wax or stearine. It appears light on a dark ground if the screen is illuminated more strongly at the back than at the front, and in the reverse case dark on a light ground. The normal flame is placed on one side of the screen, and on the other the flame to be measured, and this is displaced until the spot nearly disappears. If, *e.g.*, the distance of the normal flame from the screen is 2 decimetres, and that of the flame to be measured 8 decimetres, the latter $= 8_2 : 2_2 = 16$ candles.

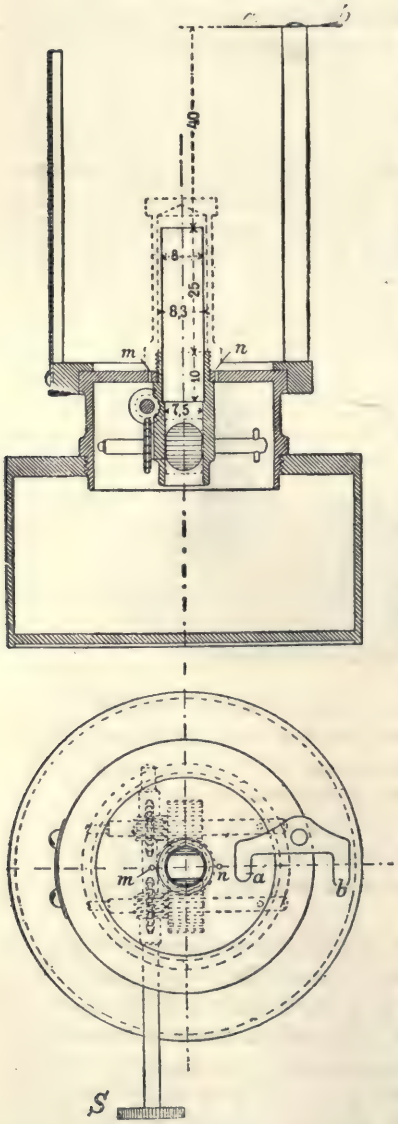
During such measurements all other sources of light must be carefully excluded.

As unit, the flame of a candle is generally used. In Germany the photometric candle has a diameter of 20 mm.; it must be accurately cylindrical, and so long that twelve candles weigh 1 kilo. The wicks must be twisted as uniformly as possible, of

twenty-four threads of cotton, and, when dry, must weigh 668 m.grammes per metre run. They are distinguished from other wicks by the introduction of a red thread. The material must be paraffine, as pure as possible, congealing not under 55°. The flame must be 50 mm. in height.

In Munich there is used as the unit a stearine candle made from a stearine containing 76 to 76·6 per cent. of carbon. It consumes hourly, according to Schilling, on an average 10·4 grammes stearine, and has a flame of 52 mm. in height. The English spermaceti candle has a wick platted of three strands, each containing seventeen threads; it consumes hourly 120 grains (7·78 grammes) spermaceti, the height of the flame being 45 mm. In France the carcel lamp is used, burning hourly 42 grammes colza oil.

Figs. 105 and 106.



The relation of these normal flames is, according to Schilling—

German Candle.	Munich Candle.	English Candle.	Carcel Lamp.
1000	887	977	102
1128	1000	1102	115
1023	907	1000	104
9826	8715	9600	1000

Monier found 1 carcel = 7·5 German candles = 7·5 bougies d'etoile = 6·5 Munich candles = 8·3 English candles. If we compare with these figures the experiments of Violle, we may be able to compare the luminosity of paraffine and spermaceti candles.

According to the newest reports of the German Normal Candle Commission, candles of paraffine, stearine, and spermaceti give almost exactly equal lights if the wicks and the height of the flame are kept alike.

The conflicting statements concerning the value of the normal candles induced Hefner-Alteneck to propose the following unit of light; it is the light of a flame burning in pure motionless atmospheric air, arising from the section of a massive wick saturated with amyl acetate. The wick completely fills a round socket of nickel silver of 8 mm. inner and 8·3 outer diameter, and of 25 mm. length. The flame is 40 mm. in height, measured from the margin of the wick-holder, and is shown by the sight-line over the angles, *a* and *b* (Figs. 105 and 106). It is arranged by looking through the point of the flame to the angles, *a* and *b*, upon which the light shows, and regulating the height of the flame by turning the milled head, *S*, so that the point of the bright nucleus of the flame just touches the line from below. The angles, *a* and *b*, are kept bright. The wick does not extend into the flame. Its nature has no effect upon the light as long as it fills up the socket, and is able to suck up the fuel in sufficient excess. Hence it must not be pressed too tightly into the socket. The wick consists of threads laid parallel to (and not

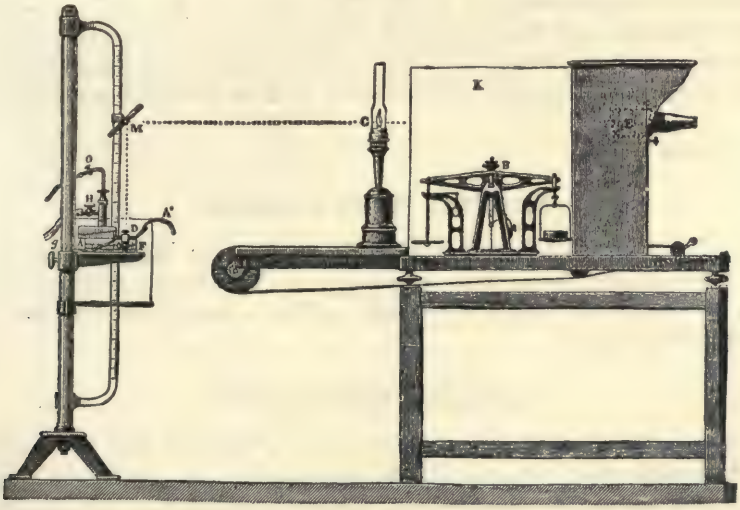
twisted or plaited) its length, so thick that it can be easily fitted to the diameter of the socket. The wick is cut level and horizontal with sharp scissors. The quantity of fuel in the lamp is not important, so long as the wick dips well in with all its threads. From time to time the wick-holder must be cleaned from a thick brown deposit. The air must be perfectly calm, as the slightest draught causes the point of the flame to rise and sink. This light-unit is equal to an English spermaceti candle at a flame-height of 43 mm.

The International Conference held in Paris in 1883–84 adopted as the unit of white light the quantity of light radiated out by 1 square centimetre of pure melted platinum at the temperature of solidification.

To produce this platinum light-unit, Violle used a platinum mlting-furnace of lime which admits an oxy-hydrogen flame to play upon the platinum through its cover. When all the platinum is fused the liquid mass has a much higher temperature than its melting-point (1775°), and the liquid metal is placed behind or under a double screen with an aperture of a certain width, through which the light falls. The screen is made of platinum or copper; it is double, and is kept cool by a stream of cold water. The light rays passing through the opening are thrown upon the photometer screen.

Fig. 107 shows the apparatus for comparing the platinum unit with the carcel lamp, as constructed by Deleuil of Paris. The carcel, C, can be moved upon a sledge

Fig. 107.



before the screen, E, of a Foucault photometer. The rays coming from both sources of light are separated by the screen, K. The apparatus for producing the platinum-unit is on the left side. F is the Deville furnace, the lid of which is pushed back in front to uncover the surface of the melted metal. D is the lid cooled with water, A and A′ the entrance and exit for water. The blowpipe is connected with the oxygen gasometer, and the supply of common coal-gas by the pipes, O and H. The whole smelting apparatus rests upon a little table, which can be fixed at any height by means of the screw, *g*. The mirror, M, reflects back upon the screen of the photometer the rays which have been let through from the cover. If the kind of light to be compared —*e.g.*, a glow-lamp—permits any desired position, the disc of the photometer is brought to bear vertically upon the crucible containing the platinum; if, as is usual, this is impracticable, the rays proceeding from the metal bath must be deflected horizontally by a mirror or a prism, as shown in Fig. 107. The co-efficient of absorption of the mirror and the prism must of course be taken into account. When the adjustment

has been effected, and the rays of both the sources to be compared fall upon the screen of the photometer, an equal illumination is obtained by displacing either the screen or one of the sources of light. The equality is very brief, as the melted metal cools, and the emission of light rapidly decreases. The measurement must be effected whilst the temperature and the light are constant. Violle gives the following comparison of the measure of light:—

	Platinum-unit.	Carcel.	French Candle.	German Candle.	English Candle.
Platinum-unit	1	2·08	16·100	16·400	18·50
Carcel	0·481	1	7·750	7·890	8·91
French stearine candle . . .	0·062	0·130	1	1·020	1·15
German normal candle . . .	0·061	0·127	0·984	1	1.13
English candle	0·054	0·112	0·870	0·886	1

Unfortunately, little is gained by proposing this international unit, as it cannot be carried about like a standard measure or weight, but must be produced afresh on every occasion, and requires preparations which will rarely be practicable. The amyl acetate lamp appears most practical, and will probably in time supersede the other units.

Illumination is effected—

1. By the combustion of solids made up in the form of candles, such as tallow, stearine, paraffine, and wax.

2. By means of liquids burnt in lamps, either (*a*) *liquid fats*, rape oil, olive oil, or train; (*b*) *volatile oils*, petroleum, solar oil, camphine (purified oil of turpentine).

3. By *gases* which are either luminous in themselves, as coal- and oil-gas, or, like water-gas, act by rendering solids incandescent, such as platinum, magnesia, zirconia, &c.

4. By electricity.

LIGHTING WITH CANDLES.

Wax candles appear not to have been made prior to the beginning of the fourth century; tallow candles made their appearance in the twelfth century; spermaceti candles in the beginning of the eighteenth century; stearine candles in 1834, and paraffine candles in 1850.*

LIGHTING WITH LAMPS.

As liquid capable of serving for the production of light we have (*a*) the fatty oils, (*b*) the volatile oils, which latter are either ethereal oils, such as camphine, products of the treatment of the tar from lignite—*e.g.*, photogen and solar oil—or oils supplied by nature (petroleum and naphtha). Of the fatty oils the most common are rape, colza, olive oil, train, and, more rarely, poppy oil.

In order to refine the fatty oils, they are mixed with 2 per cent. of sulphuric acid, or a strong solution of zinc-chloride, and well shaken up. These reagents do not attack the oil itself, but destroy all the mucilaginous and other foreign matter, and separate it out. On washing with water, the acid and the zinc-chloride are removed,

* Notwithstanding the introduction of gas and of petroleum lamps, the demand for candles is still increasing. The preparation of wicks and the process of moulding candles are mechanical rather than chemical operations; and, as much space will be required below for the introduction of matter not contained in the German edition, they are omitted. A light obtained by the combustion of magnesium wire must not be overlooked. It is certainly expensive, but it resembles solar light more closely than even the electric light, and is therefore unequalled for use in the tinctorial arts if it is required to match off colours after sunset, or in foggy or cloudy weather. If metallic magnesium can be produced more cheaply, this light will have a great future.

and the oil is thus purified. Since the rise of the paraffine and petroleum industry the importance of the fatty oils as sources of light has much declined.

Lamps were in use in pre-historical ages. Elegant as were the forms of those employed by the Greeks and Romans, their construction was technologically most imperfect. If we except a few empirically discovered improvements, such as the lamp-glass (chimney) introduced by Quinquet, and the invention of the hollow circular wicks by Argand in 1786, the construction of a normal lamp has been rendered possible by the development of chemistry—*e.g.*, the theory of combustion and illumination, the application of physical data to the supply of oil to the burner, and the determination of the illuminating power of the lamp-flame, the refining of oils, and the supply of solar oil and petroleum. In 1850 the camphine lamp was introduced, and, soon after, the elegant but costly regulators and moderators. In the fifties began a struggle of the oil-lamps among themselves, and at the same time against gas. In the sixties the petroleum-lamp appeared, and has almost entirely superseded the oil-lamp. A lamp contains the same parts as a candle—the luminiferous material and the wick. In each the material is liquid, and the difference is merely that in the candle, in the cup-shaped depression round the wick, the fat (stearine, tallow, paraffine, &c.) is burnt in a melted condition, whilst in a lamp the material is liquid at common temperatures, and requires a vessel in which the liquid fuel is contained, so as to feed the flame continuously and as equally as possible. The great variety which we see in lamps resolves itself into the character of the fuel, the form of the wick, and the manner of supplying air to the flame, whether with or without a draught; in the shape of the oil cistern, its position with respect to the wick, and in the conveyance of the oil to the wick, whether by capillarity alone or in connection with hydrostatic or mechanical pressure.

Rape oil and mineral oil, whatever the character of the latter, differ in the fact that the former at common temperatures does not evaporate. Hence it is inodorous, and cannot be ignited. Only when it has been heated to such a degree that the products of dry distillation, especially inflammable gases, are formed, do ign ion and combustion of the oil take place. Mineral oil, even the so-called "inodorous" quality of the factories, has a smell, and on prolonged exposure to the air it gradually loses weight. At higher temperatures it evaporates, and may be distilled unchanged. At a still greater heat it is gasified, and becomes chiefly illuminating gas. Refined rape oil in a properly constructed lamp burns only in a gaseous form, and completely, yielding merely the inodorous products, carbonic acid and watery vapour. Solar oil and mineral oil are mixtures of various hydrocarbons. They begin to boil at 250°, and at higher temperatures are resolved into gaseous products, and into free carbon. The proportion of carbon in mineral oils is far greater than in rape oil, as is here shown :—

Names.	Per Cent. Composition.			1 Kilo. requires O for Combustion.	1 Kilo yields :	
	Carbon.	Hydrogen.	Oxygen.	kilos.	Carbonic Acid. kilos.	Water. kilos.
Stearine	76·1	12·5	11·4	2·92	2·79	1·13
Rape oil	77·2	13·4	9·4	3·04	2·83	1·21
Tallow	78·1	11·7	9·3	2·91	2·86	1·05
Spermaceti . . .	81·6	12·8	5·6	3·14	2·99	1·15
Wax	81·8	12·7	5·5	3·14	3·00	1·14
Petroleum	85·2	14·8	—	3·45	3·12	1·33
Paraffine	85·7	14·3	—	3·43	3·14	1·29

Hence the first burns in the open air with a smoky flame, which, by the use of a draught-glass, is at once rendered of a dazzling whiteness and strongly luminous, the combustion of the excess of carbon being thus effected by the increased supply of air; whilst rape oil arrives at the flame only in a gasified condition, solar oil and the less

volatile part of petroleum, similar in its composition, enter the flame as a vapour. Mineral oil lamps must therefore be so arranged that the combustion is effected as perfectly as possible, and that no trace of the malodorous vapour escapes unconsumed.

A normal lamp, whatever its fuel, must be so constructed that it gives out a maximum of light during a certain time, and that as uniformly as possible; the light produced must also be utilised to the best advantage.

Lamps may be classified according to the manner in which the fuel arrives at the point where the light is to be evolved. Thus we have—

(1) Suction lamps, in which the oil is brought up by capillary action alone from a lower receiver. (2) Pressure lamps, in which a mechanical or physical arrangement conveys the oil to the wick. Pressure lamps are again subdivided into (*a*) *aërostatic* lamps, in which the principle of Heron's lamp comes into play; (*b*) *hydrostatic* lamps, depending on the principle of communicating tubes according to the levels of liquids of different specific gravities in connected tubes; (*c*) *static* lamps, in which the oil is

Fig. 108.

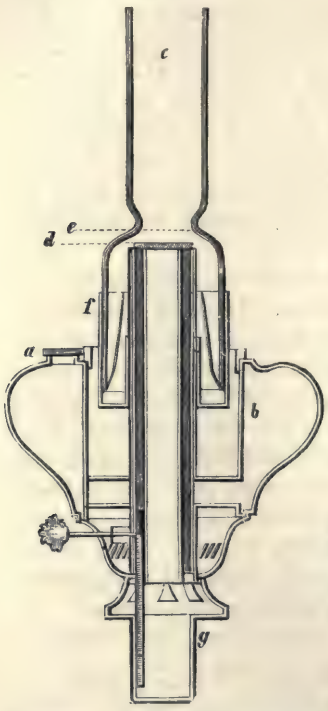


Fig. 109.

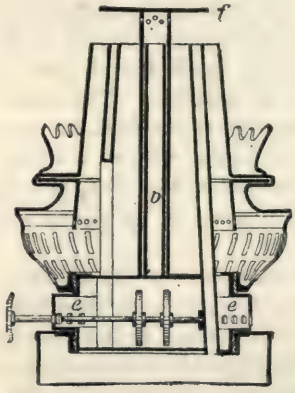
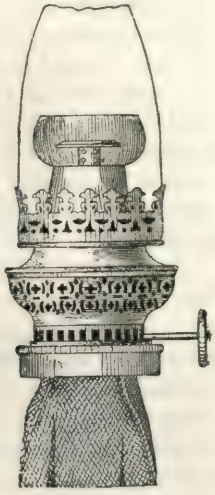


Fig. 110.



driven up by a weight or a piston, and (*d*) *mechanical* lamps, in which the oil is pumped up to the burner by means of a train of wheel work or by the action of a spring.

Mineral oil lamps always act on the principle of suction, and they are now the only kind which require to be described and figured. Of the older forms must be mentioned that designed by R. Ditmar. It consists (Fig. 108) of a metal oil-holder, *b*, which surrounds the wick-holder in the form of a ring, and is connected with the latter merely by a horizontal tube in order to convey the oil to the wick. An aperture closed by a perforated screw, *a*, serves to introduce the oil into the holder, *b*. The lamp has a circular wick and a double current of air; it has a glass chimney contracted at *e*, and resting on a movable support. The chief part of the luminous flame, which should be altogether from 6–8 centimetres in height, is above the contracted part. The oil-holder does not become appreciably heated.

In the lamp of Schuster and Baer of Berlin, intended for heavy oils (Figs. 109 and 110) the air is supplied by means of a perforated box, *e*, an air-tube, *v*, within the combustion tube and the perforated support of the disc, *f*. This lamp gives, with solar oil, a bright white, steady, and perfectly inodorous flame.

The "Imperial lamps" recently introduced give an illuminating power up to 110 candles. Their characteristic feature is that the air-pipe, *G* (Fig. 111), passes

Fig. 111.

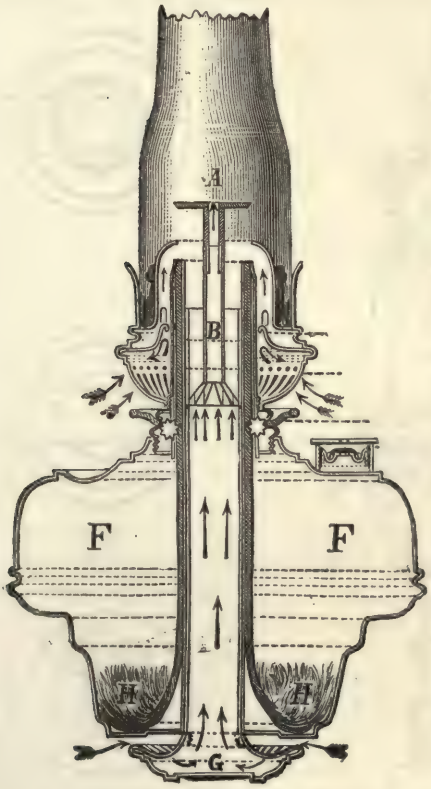
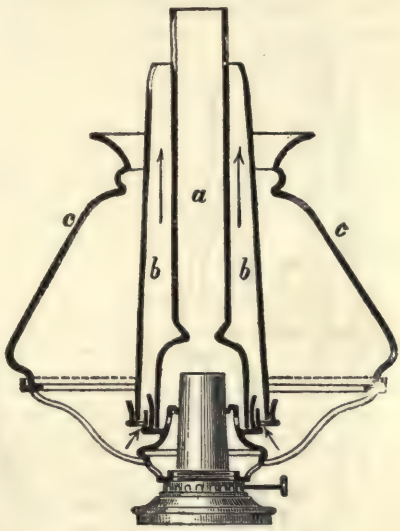


Fig. 112.



through the oil-holder, *F*, with the wick, *H*. The star-shaped piece, *B*, with the disc, *A*, regulates the distribution of air.

In study-lamps the radiant heat must be guarded against. Schuster and Baer, in their "normal hygienic lamp," surround the ordinary cylinder, *a* (Fig. 112), with a second cylinder, so that the dome, *c*, is kept cool by the current of air ascending between both.

The ligroine and sponge lamp, proposed some thirty years ago, has not come into general use.

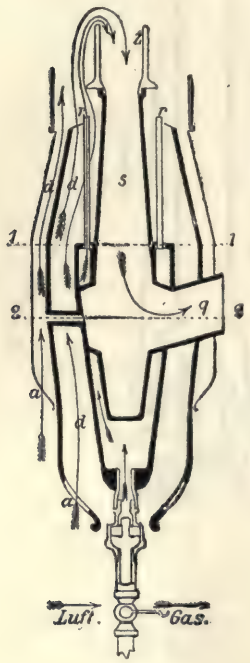
GAS LIGHTING.

Burners for gas are constructed of iron, brass, porcelain, or steatite. Those of the two latter materials are never choked in consequence of oxidation. The chief classes of burners are the following:—(1) The single-hole burner, a short, hollow cylinder, closed at top with a plate having a fine aperture. (2) The slit-burner has in its button-shaped top a cut like that made by a saw. The flame is flat, broader than high, and is hence known as the bat's-wing burner. If two such burners are inclined towards each other, so that the flames intersect each other, we have the twin-burner, which gives out more light than the two flames of which it is composed. (3) The Manchester burner—a fish-tail—has, instead of the slit of the bat's-wing, two apertures inclined towards each other at an angle of 90°. (4) In the Argand burner, chiefly used in rooms, the flame consists of a circle of small rays, each issuing from a separate orifice. (5) In the Dumas burner there is a circular slit instead of the circle of orifices. (6) In the sun-burner, a number of slit-burners are so placed that the flames coalesce.

Of prominent importance are the so-called regenerative gas-burners, in which the gas and the air are heated before ignition. The most widely known of these burners is that of Fr. Siemens (Figs. 113 to 117), consisting of several upright receivers placed one within the other. The air entering through the slits at *a* takes the way indicated by

arrows through the external regeneration cells, *d*, in order to burn outside the porcelain cylinder, *z*, with the gas escaping from the circular tubes, *r*, placed in the regenerator. The products of combustion escape in part down through the hollow porcelain

Fig. 113.



Luft = Air.

Fig. 114.

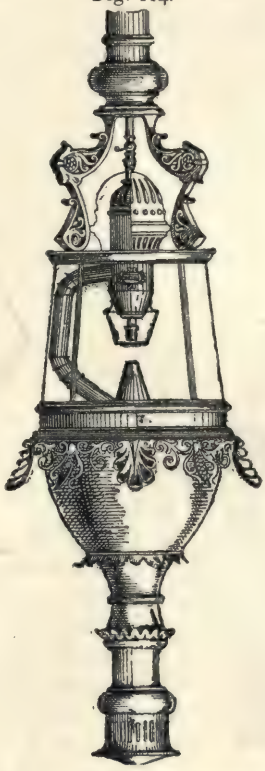


Fig. 115.

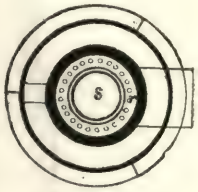


Fig. 116.

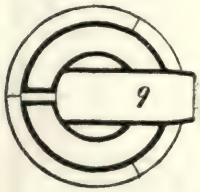
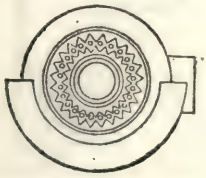


Fig. 117.



cylinder, *z*, and the internal regenerator, *s*, through the support, *g*, into the flue which (Fig. 113) leads up on the side of the main body into the chimney above the cylinder, *z*;

Fig. 118.

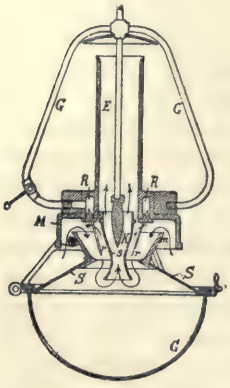


Fig. 119.

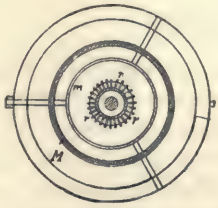


Fig. 120.

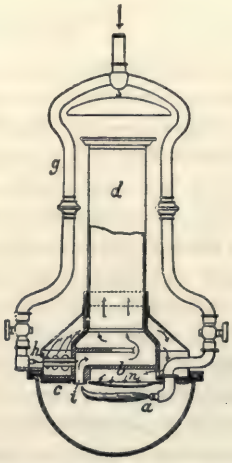
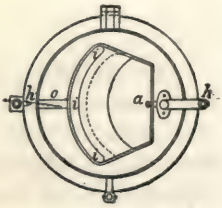


Fig. 121.



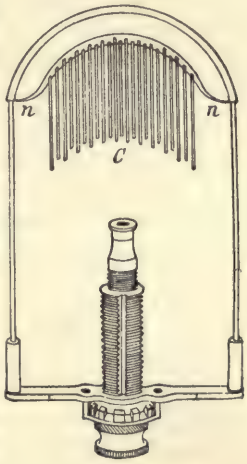
another part of the products of combustion passes directly upwards into the chimney, whilst the latter is directly heated by a part of the products of combustion; the portion drawn downwards through the regenerator, *s*, serves to heat the air and the gases.

The heated air is especially divided and conducted by means of the so-called distributing-combs placed at and above he uorifices of the gas-pipes.

When it is required to throw the light downwards, the inverted regenerative burner of Fr. Siemens is to be recommended. Here (Fig. 118) the gas-pipe, *G*, leads into the horizontal gas-ring, *R*. This has on its lower side a number of small burner tubes, *r*, screwed in or wedged in, which, as shown in Fig. 119, collect below to a smaller circle. At the lowest and narrowest point of the circle formed by the burner tubes, *r*, are their orifices, where the gas meets with the necessary air for combustion brought from below (see the arrows) into the external mantle, *M*, and, with the gas, it escapes downwards as flame. For the better joint conveyance of gas and air, the inner mantle, *m*, has at its lower end a surface whereby the transverse section of the transit is much contracted. (For further details see the inventor's English patents, Nos. 13,701 and 13,788 for 1886.)

The regenerative slit burner of Fr. Siemens has an ordinary slit burner (Figs. 120 and 121) with a steatite orifice so arranged as to give a rounded flame. This expands in the form of a shell beneath the reflector, *c*, provided with many fine apertures, whilst the products of combustion escape through the circular opening, *i*, into the cast-iron regenerator, *b*, and escape through the flue, *d*. The air drawn through the openings of the screen passes, strongly heated, in the direction of the arrows, through the bottle-shaped space, *n*, and the perforated reflector, *c*, to the flame. A part of the gas goes through the tube, *g*, to the arrangement for lighting, *h*. This apparatus surpasses in power and economy all the prior devices of Siemens as well as of others.

Fig. 122.



Regenerative burners have also been designed by J. R. Foster, and Wenham.

Auer von Welsbach deluminises coal-gas, burning it in a Bunsen burner and igniting then in a cylindrical earthen screen. In this arrangement the quantity of light decreases rapidly, and the screen is easily broken, so that the general adoption of that light is out of the question.

Fahnehjelm's "globe-light" has proved successful. A fish-tail burner is fed with water-gas, and rods of magnesia, lime, zirconia, kaolin, silica, &c., are ignited. If the iron comb, *n* (Fig. 122), supporting two rows of magnesia rods, is set up, the flame of the water-gas strikes between the rows of the rods and ignites them to whiteness, when a powerful and perfectly white light is radiated out. The mass of which the rods consist is chiefly burnt magnesia, rendered plastic by means of starch and other suitable material. The arch supporting the comb can be fixed lower or higher by means of a steel bar working on a tapped spindle.

Gillard's "Platinum Gas."—In 1846 Gillard established works in which hydrogen was obtained for illuminating purposes. The hydrogen-flame was made to play through a net-work of fine platinum wire, which was shortly heated to whiteness, and rendered luminous. It was called in Paris "platinum-gas," and has been everywhere abandoned.

Tessié du Motay obtained hydrogen by heating hydrated lime with coal. Oxygen is obtained by first heating pyrolusite with caustic soda to 450° in the air, forming sodium manganate, and then passing superheated steam over the mixture, when the reverse reaction takes place.

If the mixture of caustic soda and sesquioxide of manganese is heated in a current of air, it is again converted into sodium manganate. The ignited oxyhydrogen gas

thus obtainable was passed over small cylinders of magnesia or zirconia. The process has been everywhere abandoned.

The Drummond light, obtained by exposing caustic lime to the flame of oxyhydrogen gas, has been everywhere superseded by the electric arc-light.

H. Cohn endeavoured to find the limit at what quantity of light it is still possible to read and write without straining the eyes. He determined the time necessary, at different grades of illumination, to read 36 hook-shaped figures at 6 metres distance, stating whether the hooks were open upwards, downwards, to the right or to the left. He found that with

1 candle	0–12	hooks were read in	40–60	seconds	with very many faults
5 candles	36	„ „	48–73	„	with many faults
10 „	36	„ „	30–60	„	with some faults
20 „	36	„ „	22–26	„	correctly
50 „	36	„ „	17–25	„	as in good daylight.

He determined also that in a minute twelve lines of newspaper print could be read with ten candles, sixteen lines with fifty candles, as in the daylight; ten candles are therefore the lowest light which a work-room should have.

The following conspectus shows the cost of the chief kinds of illumination for 100-candle hours :—

How the Hourly Production of 100 Candles are required.			Thereby Evolved.		
Kind of Light.	Quantity.	Price in Shillings and 100ths of a Shilling.	Water. kilos.	Carbonic Acid. cub. met.	Heat. thermic-units.
Electricity, arc light	0·09–0·25 h.p.	0·060–0·120	—	traces	57–158
„ glow light	0·46–0·85 „	0·150–0·300	—	—	290–536
Gas, Siemens regen. burner	0·35–0·56 c.m.	0·063–0·101	—	—	1,500
„ Argand burner	0·8–(2)	0·144–0·360	0·86	0·46	4,860
„ two-hole burner	0·2–(8)	0·360–1·440	2·14	1·14	12,150
Petroleum, round burner	0·20	0·040	0·22	0·32	2,400
„ flat „	0·60	0·120	0·80	0·95	7,200
Solar oil, Schuster and Baer's lamp	0·28	0·062	0·37	0·44	3,360
„ flat	0·60	0·132	0·80	0·95	7,200
Rape oil (carcel)	0·43	0·413	0·52	0·61	4,200
„ (study lamp)	0·70	0·672	0·85	1·00	6,800
Paraffine	0·77	1·390	0·99	1·22	9,200
Spermaceti	0·77	2·700	0·89	1·17	7,960
Wax	0·77	3·080	0·88	1·18	7,960
Stearine	0·92	1·660	1·04	1·30	8,940
Tallow	1·00	1·600	1·05	1·45	9,700

As regards the pollution of the air, carbonic acid and watery vapour have to be first considered. From the figures in the table, it follows that solar oil and mineral oil give off the least carbonic acid and watery vapour, gas and tallow the most. In the Siemens regenerative burner they are conveyed outside.

A contamination of the air with carbon monoxide and hydrocarbons is not to be apprehended in the case of burners furnished with cylinders. Petroleum lamps smell only if the flame is much too large or too small, or if the lamp is not kept clean. With free-burning flames, as the air is rarely quite steady, a contamination of the atmosphere with carbon monoxide is likely to occur. Coal-gas always contains sulphur, and yields on combustion sulphurous and sulphuric acids, which act injuriously upon window-plants, possibly upon the inhabitants, as well as upon books, pictures, articles of metal, and upon curtains, &c. The mineral oils of commerce often contain sulphur. Ordinary gas-lighting occasions more heat than oil-lighting. Among candles, those of tallow are the least advantageous.

Where economy is considered, solar oil, and especially petroleum, are to be employed;

gas-lighting is dearer, and pollutes the air more, but it is convenient. When other circumstances allow, gas-lights, with regenerative burners or electric glow-lamps, are preferable, as they do not pollute the air, and give the least heat. For a study—or generally a working light—the author prefers a good mineral oil lamp as giving the steadiest flame.

ELECTRIC LIGHT.

The electric light is suited for large halls and gardens, where beauty is to be considered rather than economy. For lighting up streets, manufactories, and railway stations, it is cheaper than gas only where a cheap motive power is available.

In estimating the arc-light, we must consider that with continuous currents the positive carbon, which is always placed as the upper one, takes the form of a blunt point, often with a small hollow in place of its point; whilst the lower, negative carbon, remains pointed, or has in any case a very convex summit. At the lower point only a small part is luminous, whilst by far the chief portion of the light comes from the internal side of the concavity of the upper carbon, and is, of course, thrown entirely downwards. This is best seen if the light is enclosed in a globe of translucent glass. The upper part of the globe is comparatively dark; the lower very luminous except quite at its bottom, where the shadow of the lower carbon is visible. The limits between the two zones are never horizontal, but more or less slanting, especially when the carbons are not quite straight. It is seen at once that measurements of the free light in a horizontal direction—as was formerly customary—give very uncertain results. According as the naked light happened to be measured from the one side or the other, it might be taken in the dark or the light zone.

Fig. 123.

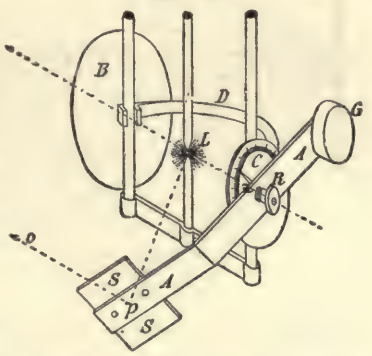


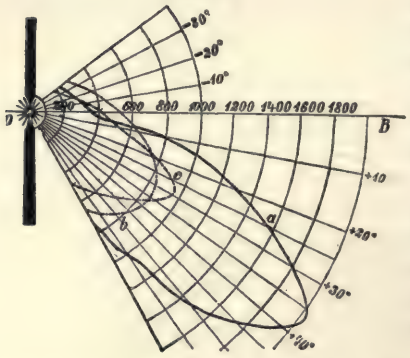
Fig. 123 shows the little apparatus with which such measurements are conducted by the firm of Siemens & Halske. It consists chiefly of a small mirror, *S*, fixed to a movable curved arm, *A*. The supporter of the entire apparatus, *D*, can be fixed to an electric lamp (of which only the upper part is shown) by means of the screw, *R*. This is effected so that the prolongation of the axle on which the arm, *A*, turns, passes through the arc. This prolongation is brought into the axis of the photometer (placed at a distance), to which the arrows in the figure are pointing. The mirror, *S*, in every one of its positions is equidistant from the arc, and so inclined that it reflects to the photometer the rays falling from the arc upon its middle always at a right angle, *L*, *p*, *o*. Between the photometer and the arc is the metal disc, *B*, which prevents the passage of the direct rays to the photometer. On the other hand, the cone of rays from the image of the arc in the mirror arrives unhindered at the photometer. The inclination to the horizon at which these rays are emitted corresponds to the inclination of the arm, *A*. It is read off on the index, *z*, and the graduated dial, *C*. The counterpoise, *G*, serves for the mirror and the arm, *A*, which is kept in each of its positions by a slight friction. In order to deduce the absolute value from the measured results, the co-efficient of absorption of the mirror must be ascertained and taken into account. As the angle of reflection is always the same, this co-efficient does not vary; it may be determined once for all. For this purpose the mirror is turned downwards, and the lamp is turned 90° round the perpendicular, so that the rays fall directly from the arc towards the photometer in the same plane as they are to be previously or afterwards measured by means of the mirror, also in horizontal radiation. The very trifling

alteration which the angle of incidence of the rays undergoes in the photometer in consequence of the lateral application of the mirror is measured simultaneously, and therefore compensated.

In Fig. 124 the intensities of light are shown graphically in the curve, *a*; they are measured by means of the apparatus Fig. 123, from a light having 9·4 ampères strength of current and 45 volts difference of tension at the carbons. The upper carbon is 11 mm. and the lower 9 mm. in thickness. The line *OB* shows the horizontal, and *O* the source of light. The strengths of the light from *O* onwards are plotted out upon lines which have the same inclination as *OB*. The values given are the means of many measurements; indeed, in the measurement of the electric light we must never be content with single observations, but must collect copious experience to escape very glaring errors. From the course of this curve we see at once that the maximum of light is given off at an angle of about 37° with the horizon, where it is more than six times greater than in the horizontal plane.

But the case is complicated by the circumstance that in practical use the question becomes involved by the enclosure of the light in translucent globes or lanterns. These are used, not merely to prevent dazzling, but chiefly because all the lower parts of the lamp, every spoke of the lamp, and every irregularity in clear glass would throw very sharp and ugly shadows. In so-called mat and alabaster glass the loss thus occasioned is 15 per cent., in opal glass above 20, and milk glass above 30 per cent. This loss of light is greatest in the direction of the strongest rays, the inequalities of the illumination being thus equalised at the cost of the maxima.

Fig. 124.



Von Hefener-Alteneck made accurate experiments with a larger mirror apparatus. The curve *c* (Fig. 124) thus ascertained corresponds to a lantern of ground glass; the curve *b* to a new globe of a glass not very opaque. Reflectors placed above are of little value, as the smallest part of the light is thrown upwards, so that the gain is trifling in comparison with the inconvenience and the expense.

With reference to the values determined by the Paris Commission, and to the assumption that 1 cubic metre of coal-gas yields hourly 1 horse-power, Voit has calculated the following table:—

1 cubic metre of gas yields—		
in a one-hole burner		45 units light
in an Argand burner		70 „
in a small Siemens burner		141 „
in a large „ „		145 „
in glow-lamps	80–160 (mean)	110 „
in arc-lamps	250–750 „	490 „

Hence gas is used for lighting more appropriately (though not always more cheaply) if it is burnt in a gas engine which drives a dynamo and feeds an electric lamp than if it is used directly in a burner.

The disposable work in gas is not entirely utilised as light, but to a great degree as heat. From other considerations, it appears that a body at higher temperatures emits a greater proportion of external work as light, and a smaller as heat. It may therefore be understood that 1 cubic metre of gas can develop larger quantities of light at the higher temperatures of the above table.

We must notice the *intensity of light*. Two sources of light may send out the same *quantity of light*, but one of them has a large and the other a small surface, so that the former, from a given unit of surface, emits a smaller quantity of light than the other. This light sent out from a superficial unit is called the *intensity* of the source of light. If, for the sake of simplicity, we assume that each part of the surface of the two sources of light emits the same quantity, we find the intensity by dividing the total light emitted by the surface of the luminous body. The rays of the sun passing through an orifice of 0·9 mm. diameter correspond, according to Sir W. Thomson, to 126 candles = about 20,000 candles per square centimetre. Moonlight is equal to the light of a normal candle at the distance of 2·3 metres.

In this manner the luminosity of 1 square centimetre of surface is found:—

Single-hole burner	0·06 candles
Argand	0·30 „
Small Siemens	0·38 „
Large „	0·60 „
Glow-lamps *	40·00 „
Arc-lamps	484·00 „

* The glow-lamp, or incandescent lamp, is a mode of obtaining light by electric action perfectly distinct from the arc light. It is well known that if in a good electric conductor, through which a current is being passed, there is introduced a short piece, having a very high resistance, we have in such a short piece, in accordance with Joule's law, a very considerable evolution of heat, which, if the current is sufficiently powerful, renders it incandescent and luminous. If such a short and resistant piece is enclosed in a vacuum, and if it is relatively long in proportion to its diameter, so as to increase the resistance, we have, in substance, the glow lamp. A variety of practical conditions are essential—the vacuum, which should be very high, has to be enclosed in a glass globe, or, more commonly, a pear-shaped vessel. This vessel must be so constructed that the air may be readily exhausted, and be then sealed up so as to allow no entrance of air. The two wires are also sealed into the neck of the vessel in such a manner that the current can pass from the one to the other only by traversing the filament which is to be rendered incandescent. The nature and preparation of this filament have been the critical points of the invention. The earliest glow-lamps constructed, those, *e.g.*, of Lontin de Clangy, King, and Lodyguine, had spiral platinum wires, as had also those of Edison in his first attempts. The conclusion was soon reached that a filament of carbon was preferable to one of metal, on account of its higher durability. Wood charcoal, retort charcoal, &c., were successively tried, and in 1879 Edison prepared filaments from carbonised bamboo. Other materials have since been used by Swan, Lane Fox, Crookes, and others, such as gelatine, collodion, cotton, &c., the main condition being the production of a fibre equally thick and strong throughout its entire length. Before carbonising, therefore, the fibres are carefully examined with an apparatus capable of indicating the hundredth of a millimetre. They are then charred in a fire-clay muffle, or in a Hessian crucible, every layer of fibres being covered with charcoal dust or graphite. The crucible is then filled up with the same material, and the lid is carefully luted on. When the luting is dry the crucibles are placed in the furnace and ignited for five hours to 1000°–1200°. The higher and more uniform the heat the better is the quality of the filaments. The specific resistances of the different materials, that of mercury being taken = 1, are—

Charred bamboo fibre	62·56
Prepared „	50·00 29·00
Unprepared collodion carbon	39·90
Prepared „	22·00
Chemical retort carbon	7·17

Lamps are classified according to their luminous power. They are generally made to give the light of 8, 10, 16, 20, 25, and 32 candles, those of 16-candle power being in greatest demand. In gauging the lamps, accurate photometry is essential. Silvanus Thompson, instead of the grease spot on the screen, uses two pieces of paraffine or milk glass, between which is laid a polished slip of sheet silver. This arrangement is more convenient and more sensitive than the fat spot. The duration, or, as it is technically called, the lifetime, of a glow-lamp varies, according to the current used, from 300 to 2400 hours. The great recommendation of the glow-lamp is its universal applicability. It gives off very little heat, does not contaminate the air with the products of combustion, and reduces the risk of fire to a minimum. As compared with the arc light, the glow-lamp has the advantage of absolute steadiness.

SECTION II.

METALLURGY.

ONLY the chemical processes of metallurgy can here be discussed, as the mechanical arrangements form a part of mechanical technology.

Few metals occur native; most of them are found in the mineral kingdom in chemical combinations known as ores and as—

(1) *Elements: e.g.*, gold, platinum, bismuth, copper.

(2) *Chlorides and fluorides:* Compounds of the monovalent elements chlorine or fluorine with metals (if heated with sulphuric acid, they give off HCl or HF)—*e.g.*, sodium chloride, carnallite, cryolite.

(3) *Oxides:* Oxygen compounds of the metals with or without hydrogen—*e.g.*, red copper ore, hydroferrite, and anhydroferrite.

(4) *Sulphides* and corresponding compounds: Sulphur and arsenic-combinations of the metals (if laid on ignited charcoal, they give off SO_2 or the odour of arsenic—*e.g.*, iron-pyrites, galena, blende, proustite).

(5) *Sulphates:* Compounds of the general formula $R^{II}SO_4$ (if melted upon charcoal with soda, they give sodium sulphide; heated with soda in a tube, their watery solution gives with $BaCl_2$, $BaSO_4$ insoluble in hydrochloric acid—*e.g.*, gypsum and heavy-spar).

(6) *Borates:* If heated on a platinum wire with H_2SO_4, they tinge the edge of the flame a fine green—*e.g.*, boracite.

(7) *Nitrates:* Compounds of the general formula R_1NO_3 (they are soluble in water, and deflagrate on charcoal—*e.g.*, cubic nitre).

Dressing.—Ores mostly require to be broken up and separated from foreign ores and from the accompanying earthy or stony masses (gangue). This separation is, of course, mechanical, and is often begun at the mine. The ores are generally sorted into three heaps: the first heap is so rich that it can be at once smelted; the second heap contains medium ore, which, before smelting, has to be further freed from mechanical impurities; whilst the third heap consists chiefly of gangue, so that the little metal which it contains is not worth the cost of extraction.

Preparation.—By the above-mentioned dressing the ores are rendered rich enough for further treatment. Before smelting, a preparation of the ores is often required, which in some cases consists of exposure to the air—*weathering;* or in heating without access of air—*burning;* or heating with access of air—*roasting.* Weathering effects a mechanical separation of the clay, shales, &c., from the nodules of ore, as it is chiefly done in iron ores and calamine; sometimes it effects also an oxidation of iron ores and of accompanying pyrites to form copperas, which is then washed away by the rain. Burning or calcination loosens the texture of certain ores, such as ironstone, calamine, copper-shales, by expelling volatile matter such as water, carbon dioxide, bitumens, or merely by the expansive power of heat. Roasting effects merely an oxidation—*e.g.*, magnetic iron ore; or a simultaneous expulsion of certain matters. Blende, *e.g.*, on roasting, yields zinc oxide and SO_2 (*see* Zinc), arsenides evolve arsenious acid, and cinnabar is split up into mercury and sulphurous acid. Ores are in some cases roasted with the addition of common salt (*see* Silver).

Smelting.—Single kinds of ore are rarely smelted by themselves; in general, richer

and poorer qualities are mixed together, so as to bring the whole to a medium standard. Attention has also to be paid to the portions of gangue which still accompany the ore, so that the slag produced may be of a suitable quality. For this purpose, certain materials are in most cases added, which are known as *roasting materials* (charcoal, coke, coal, quicklime, and common salt); or as *fluxes*, quartz, and certain silicates (hornblende, felspar, augite, chlorite, and old slags); calcareous minerals, such as limestone, fluor-spar, gypsum, and heavy spar; aluminous minerals, such as clay slate and clay, &c.; saline fluxes, such as potash, soda, borax, salt-cake, soda, saltpetre; metallic additions, such as iron (in the decomposition of cinnabar and galena), zinc (for the separation of silver from lead), arsenic (for increasing the proportion of nickel and cobalt in speiss), iron-slack, red and brown hæmatite in the puddling process; additions rich in such materials, as puddling-slags, rich in ferrous oxide, and which act either by their proportion of oxygen (in puddling iron), or by their iron as a precipitant (in separating lead from galena). Fluxes merely promote the separation of the metal by increasing the fluidity of the melted mass, so that the particles of metal may unite more easily. They may be arranged in three classes—(1) such as have little chemical action, but merely promote fusibility, such as fluor-spar, borax, common salt; (2) those which in addition have a reducing action, such as black flux (a mixture of tartar and saltpetre); (3) those which act by absorbing either acids or bases.

Mixing is the operation by which the ore and the additional materials and fluxes are mixed together. The quantity used in a period of twelve to twenty-four hours is called the charge.

Furnace Products.—The products of the smelting process are either—(1) *Metals* (educts). The degree of purity in the precious metals is expressed by *fine* (fine silver, fine gold); in the base metals we speak of raw or crude metal, whilst a higher grade of purity is indicated as *refined.* (2) Such furnace products as are not already contained in the ores, but are formed by the reactions taking place during smelting, are many of them articles of commerce, such as hard lead (antimonial and arsenical), spiegeleisen, the various sorts of steel (such as Bessemer steel, cement steel, &c.), the arsenical products (arsenious acid, orpiment, and realgar), antimony sulphide, &c. There are often also by-products, which, if capable of further elaboration, are (3) intermediate products, or, in the opposite case, (4) waste or dross.

The intermediate products are alloys, "*teller* silver," consisting of silver, copper, and lead; work-lead, lead containing some silver or copper; black copper, consisting of copper with iron and lead, &c.; arsenides, speises; carbides, crude iron and steel; and oxides, such as litharge.

Slags.—The chief waste products of smelting-furnaces are slags, vitreous masses resulting from most smelting processes, the most important of which are silicates, *i.e.*, compounds of silica with earths (especially lime, magnesia, alumina) and with metallic oxides (ferrous and manganous oxides). In smelting processes they are formed from the impurities never absent in the ores and in the admixtures, and subserve the important task of protecting the metal as it is liberated from the oxidising action of the blast. Their nature depends on their proportion of silica, whence they are divided into sub-, mono-, bi-, and tri-silicates. The proportion of the oxygen of the silica to that in the bases is as follows:—

Proportion of O. B. : A.	Metallurgical Name.	Old Equivalent.	New Atomic Weights.	
		Dualistic Formula.		Molecular Formula.
1 : 3	Trisilicate .	$\dot{R}_2\ddot{S}i_3$ or $\dddot{R}_2\ddot{S}i_9$	$2R^{II}O.3SiO_2$ or $2R^{VI}{}_2O_3.9SiO_2$	$R^{II}{}_2Si_3O_8$ or $R^{VI}{}_4Si_9O_{24}$
1 : 2	Bisilicate . .	$\dot{R}\ddot{S}i$ or $\ddot{R}\ddot{S}i_2$	$R^{II}O.SiO_2$ or $R_2O_3.3SiO_2$	$R^{II}SiO_3$ or $R^{VI}{}_2Si_3O_9$
1 : 1½	Sesquisilicate .	$\dot{R}_4\ddot{S}i_3$ or $\dddot{R}_4\ddot{S}i_9$	$4R^{II}O.3SiO_2$ or $4R_2O_3.9SiO_2$	$R^{II}{}_4Si_3O_{10}$ or $R^{VI}{}_8Si_9O_{30}$
1 : 1	Monosilicate .	$\dot{R}_2\ddot{S}i$ or $\ddot{R}_2\ddot{S}i_2$	$2R^{II}O.SiO_2$ or $2R_2O_3.3SiO_2$	$R^{II}{}_2SiO_4$ or $R^{VI}{}_4Si_3O_{12}$
1½ : 1	Subsilicate .	$\dot{R}_3\ddot{S}i$ or $\ddot{R}\ddot{S}i$	$3R^{II}O.SiO_2$ or $R_2O_3.SiO_2$	$R^{II}{}_3SiO_5$ or $R^{VI}{}_2SiO_5$

Whilst in slags the degree of silication does not exceed the stage of a trisilicate, and it is not yet ascertained whether trisilicates do not owe their high percentage of silica to the presence of quartz, subsilicates may occur of various capacities of saturation. Excesses of infusible bases, *e.g.*, lime, are not uniformly distributed in the slag. Aluminates are more rarely formed.

Slags are either vitreous or crystalline. From the latter, crystalline silicates often separate, which exactly agree with natural minerals, *e.g.*, augite, olivine, Wollastonite, mica, idocrase, chrysolite, felspar, &c. The mixtures of the monosilicates generally yield easily fusible (basic) silicates, whilst the bi- and tri-silicates are acid, and solidify less readily. The phosphatic slags are of the greatest importance.

If a slag is to have an appropriate composition it should be—(1) Specifically lighter than the product to be obtained, so that it may cover the surface. (2) It must be homogeneous throughout, as otherwise the smelting process is not normal. (3) It must be easily fusible, so that the particles of metal when separated out may easily sink down through the liquid mass. (4) A chemical composition such that the slag cannot react upon the product obtained.

Properties of Metals.—The extraction of the various metals depends essentially on their properties, and in the first place on their melting and boiling points. Arsenic, *e.g.*, melts only under pressure and not below redness, whilst it sublimes at 450°; it is therefore separated by distillation, not by smelting. Cadmium distils sooner than zinc, and can therefore be removed from the latter by a separate condensation of the portion which first volatilises. Cobalt, manganese, and platinum require the highest temperatures for fusion. Even very small traces of foreign substances may affect the melting-point, as may be seen in the subjoined table:—

——	Melting-point.	Boiling-point.	Specific Heat, 0–100°.	Latent Melting Heat. Heat-units.	Heat of Combustion.		Sp. Gr.
					Product of Combustion.	Heat-units per Kilo.	
Aluminium	600–850°	above whiteness	0·210	—	—	—	2·60
Antimony	425–450	1040–1050°	0·050	—	—	—	6·70
Arsenic	—	450	0·076	—	As_2O_3	1030	5·70
Lead	326–335	1450–1600	0·032	5·8	PbO	243	11·40
Cadmium	310–320	720–772	0·055	13·7	—	—	8·60
Iron, pure	1600–1800	—	0·114	—	FeO	1353	7·90
„ white, cast	1050–1100	—	—	33·0	—	—	7·60
„ grey	1100–1275	—	—	23·0	—	—	7·10
„ steel	1300–1400	—	0·118	—	—	—	7·70
Gold	1035–1250	—	0·032	—	—	—	19·30
Potassium	62	719–731	—	—	K_2O	1745	0·87
Cobalt	1500–1800	—	0·107	—	—	—	8·60
Copper	1050–1300	—	0·093	—	Cu_2O / CuO	321 / 593	8·90
Magnesium	700–800	above whiteness	0·245	—	MgO	6078	1·70
Manganese	1900	—	0·122	—	—	—	8·00
Sodium	96	861–954	—	—	Na_2O	3293	0·98
Nickel	1400–1600	—	0·109	—	—	—	8·90
Platinum	1775–2000	—	0·032	27·2	—	—	21·50
Mercury	−38·5	357	0·034	2·8	HgO	153	13·60
Silver	954–1040	—	0·056	21·1	Ag_2O	27	10·50
Bismuth	260–270	1090–1450	0·030	12·6	Bi_2O_3	96	9·80
Zinc	412–420	930–954	0·094	28·1	ZnO	1300	7·10
Tin	227–230	—	0·056	13·3	SnO	574	7·30

The specific heat of the metals generally increases with the temperature. Unfortunately, the determinations at high temperatures are either very uncertain or altogether wanting. Thus Byström, *e.g.*, found for iron at 1400° 0·403, whilst Pionchon found considerable variations in its specific heat. The latent melting heat

and the combustion or reduction heats are known only for few metals, and even these determinations can only be regarded as approximative. We are therefore still far from being able to calculate the various metallurgical processes, though we see from the table that lead, bismuth, and tin are easily obtained, and that the separation of mercury is easier than that of zinc.

If lead is reduced by carbon, with the formation of carbon monoxide, we have for lead, $-PbO + C = Pb + CO - (206 \times 243 = 50{,}000) + 29{,}000 = -21{,}000$ heat-units, therefore, for 206 kilos. of lead we need only 21,000 heat-units. But for magnesium, $MgO + C = Mg + CO - 146{,}000 + 29{,}000 = -117{,}000$ heat-units. In fact, the reduction of magnesia by charcoal or coke is practically impossible. For zinc we have: $ZnO + C = Zn + CO - 85{,}000 + 29{,}000 = -56{,}000$ heat-units. For mercury only $HgO + C = Hg + CO - 30{,}500 + 29{,}000 = -1500$ heat-units, so that in this case scarcely any heat is required.

For accurate determinations the specific heats of the metals must be known at all temperatures, as also the specific and latent heat of the residues, especially the slags, the latent boiling-heat of the zinc, &c., which are not yet determined.

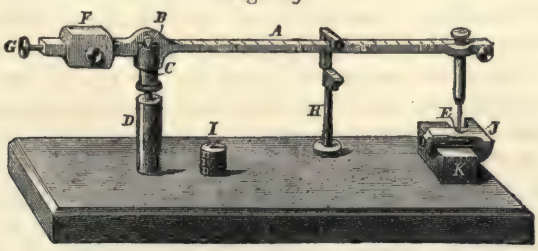
The thermo-conductivity of the metals is for a plate of 1 mm. in thickness for each 1° difference of temperature of the two sides and 1 square metre per second, in heat units :—

Metal.	Temperature.	Conductivity.	Temperature.	Conductivity.
Aluminium	0°	34·4	100°	36·2
Antimony	0	4·2	100	4·0
Lead	0	8·4	100	7·6
Cadmium	0	22·0	100	20·4
Iron	0	19·9	100	14·2
,, wrought, &c.	0	20·7	100	15·7*
Copper	0	98·2	100	83·3
Silver	0	109·6		
Bismuth	0	1·8	100	1·6
Zinc	0	13·5		
Tin	—	15·3	100	14·2
(Glass	60	0·045)		

The hardness of metals, as shown in their resistance to cutting, filing, boring, turning, and planing, is given below, the hardness of lead being taken as unity :—

Lead	1·00	Aluminium	17·30
Tin	1·73	Copper	19·30
Bismuth	3·34	Platinum	24·00
Cadmium	6·95	Wrought iron	60·70
Gold	10·70	Steel	61·40
Zinc	11·70	Cast iron, grey	64·00
Silver	13·30		

Fig. 125.



Turner, for determining the hardness of metals, uses the arm of a lever, *A*, exactly brought into equilibrium by the counterpoise, *F*, and the screw, *G* (Fig. 125), upon the

* At 275° = 12·4 heat-units.

blade, *B*. The supporter, *C*, rotates upon *D*, so that the diamond point, *E*, can be pushed laterally on the piece of metal in question, *J*, which is held by *K*. The diamond point is loaded by means of the weights, *H* and *I*, so that it leaves a distinct scratch upon the metals. Results:—

	Hardness according to Mohs.		Weight, grammes.
Steatite	1·0	...	1·0
Lead	1·5	...	1·0
Tin	2·0	...	2·5
Rock salt	2·0	...	4·0
Zinc	2·5	...	6·0
Copper, pure	2·5	...	8·0
Calc. spar	3·0	...	12·0
Soft iron	—	...	15·0
Fluor spar	4·0	...	19·0
Steel for wheels	4–5	...	20–24
Soft cast iron	4–5	...	20–24
Apatite	5·0	...	34·0
Hardest cast iron	—	...	72·0

The resistance of the most important metals to rupture is expressed in kilos. for 1 square mm. section as follows, according to Hugo Fischer:—

Tin	1	Silver	17
Lead	1	Platinum	22
Gold	11	Copper	24
Zinc	13	Iron	30
Aluminum	14	Nickel	48
Magnesium	14	Steel	80

The resistance to pressure in kilos. per square mm. is—

Lead	5
Bar iron	30
Copper	57
Steel	55–79

The hardness and tenacity of metals are often greatly modified by small admixtures and also by mechanical treatment; most metals are rendered harder and more tenacious by rolling, hammering, and drawing. This is the case with brass, iron, and platinum; less so with copper, silver, and gold, and not at all with tin and lead. As increased hardness often means increased brittleness, it is sometimes necessary, in the mechanical manipulation of iron and brass, to heat the metal under treatment from time to time, so as to render it again soft and ductile. (1) If hardness accompanied by elasticity is to be obtained, the metal is hammered, rolled, or drawn in the cold. (2) The influence which the speed of cooling after ignition or fusion has upon the hardness of a metal is particularly manifested in the case of steel and cast iron. (3) The temperature to which the metal is raised before casting is not without influence upon the hardness. If, *e.g.*, tin is heated to incipient redness and then speedily cooled, the objects cast become hard and sonorous; hence tin for tin-foil, tin-paper, &c., which must be soft and flexible, must not be heated above the melting-point.

Very closely connected with the crystalline nature and hardness of metals come malleability and ductility, collectively known as pliancy. This signifies the property of metals to spread out into thin sheets under the hammer or between rollers. For this purpose a certain softness is necessary, so that the metal may yield to a moderate pressure or thrust, yielding to the force at the point of attack, but tenacity is also needed to prevent the metal from losing its continuity. A hard, tenacious metal is pliant only when tenacity and hardness are in the right proportion. The highest degree of pliability is found in metals like silver, gold, and soft wrought iron. Soft-

ness, with deficient tenacity, as in lead, does not produce pliability. Antimony and bismuth are brittle.

In order to convert the malleable metals into sheets they are beaten out with the hammer or rolled between steel and chilled iron rollers. Those metals which can be rolled are also capable of being drawn into wire, but the degree of ductility does not always coincide with their degree of malleability or of being rolled. The metals are the most malleable, rollable, or ductile in the following decreasing order:—

Rollable.	Malleable.	Ductile.
Gold	Lead	Platinum
Silver	Tin	Silver
Aluminium	Gold	Iron
Copper	Silver	Copper
Tin	Aluminium	Gold
Platinum	Copper	Aluminium
Lead	Platinum	Nickel
Zinc	Iron	Zinc
Iron		Tin
Nickel		Lead

Closely connected with tenacity is the resistance to mechanical wear and tear, *e.g.*, friction. This resistance is high in steel, and in cast-iron poor in silicon and rapidly cooled on casting; medium in wrought iron and in cast-iron cooled normally, in platinum, silver, gold and aluminium; slight in zinc, lead, and tin. The power of resistance can be increased by suitable alloying with other metals, as lead with antimony, silver and gold with copper.

Certain malleable metals, such as soft iron, nickel, and platinum, can be welded, *i.e.*, pieces of such metals after being softened by heat to a certain degree can be united into one piece by hammering and pressure. This can be effected in other metals only by the use of a suitable solder.

IRON.

The most important iron-ores (iron stones) of commerce are:—

(1) *Magnetic Ironstone* (Fe_3O_4); it contains 72 per cent. of iron and is very widely distributed, especially in northern countries, Canada, the United States, Russia, Norway, and Sweden, in the crystalline slate formation. From this ore is obtained the celebrated Swedish iron, *e.g.*, that of Dannemora. Frequently it is accompanied by pyrites, galena, copper pyrites, apatite, and other minerals, which reduce its value as an iron ore. It is known by its black streak.

(2) *Red Ironstone* and *Specular Iron* (Fe_2O_3) contains 69 per cent. of iron. Red ironstone, the massive or earthy variety of native ferric oxide, occurs in beds in primitive formations and in quartz, granite, &c. It occurs also in transition formations, and, according to its physical properties, it is known as hæmatite, iron-ochre, &c. It is found mixed with silica (chamoisite), with alumina (red-clay iron ore), with compounds of lime (minette). Iron glance is crystalline ferric oxide; its most important deposit is in Elba. All the red iron ores have a more or less decided iron colour and always a *red streak*.

(3) *Iron Spar* ($FeCO_3$ with 48 per cent. of iron) contains almost invariably larger or smaller proportions of manganese carbonate. It occurs in Styria and in Carinthia. Kidney-shaped or globular iron spar is known as spherosiderite. It is also met with as coaly iron ore, or black band (with 35 to 40 per cent. of iron). It is a mixture of iron spar with coal and clay-slate deposited in the upper beds of the carboniferous formation (Scotland, Westphalia). Clay ironstone, or clay band, especially in England, Scotland, Westphalia, Silesia, and the Banate, is an intimate mixture of iron spar with clayey minerals.

(4) Iron spar, when exposed to the action of air and of water containing carbonic

acid, forms, as secondary products, *brown iron ores* ($H_2Fe_2O_4$ to $H_6Fe_2O_6$), which, according to their physical properties, bear the names lepido-crocite, pyrosiderite, and stilpnosiderite. These ores often contain calcium carbonate, silica, clay, &c.

(5) *Bean ore*, globular grains formed of concentric layers, occurs in some parts of Germany and France in the jura formation. It consists either of silica, ferrous oxide and water, or of brown hæmatite and siliceous clay.

(6) *Bog iron ore* (limonite, meadow-ore) is found in the alluvium of the North German Plain, in Holland, Denmark, Poland, and Southern Sweden, in peat bogs, beneath the grass of meadows, and at the bottom of lakes. It is found in tuberous and muddy masses of a brown or black colour, and consists of hydrated ferrous and ferric oxides, manganic oxide, phosphoric acid, organic matter, and sand. The iron which it yields is well suited for castings, as it is very fluid and fills the moulds well.

(7) *Franklinite* ($Fe_2O_3(ZnOMnO)$, with 45 per cent. of iron, 21 per cent. of zinc, and 9 of manganese, is used as an iron ore in New Jersey, yielding also zinc.

From a metallurgical point of view, iron ores are classified according as they are easy or difficult to reduce and smelt. Among the former rank those which, after a preparatory roasting, have a porous texture, so that they are easily reduced and smelted in the furnace. This is the case with iron spar and brown ores, which lose on roasting carbon dioxide and water respectively. Specular iron, red hæmatite, and magnetic ore are hard to reduce.

The burnt ores from sulphuric acid works, after their copper, zinc, and silver have been extracted in the moist way, are smelted for grey cast iron.

(1) Crude Iron.

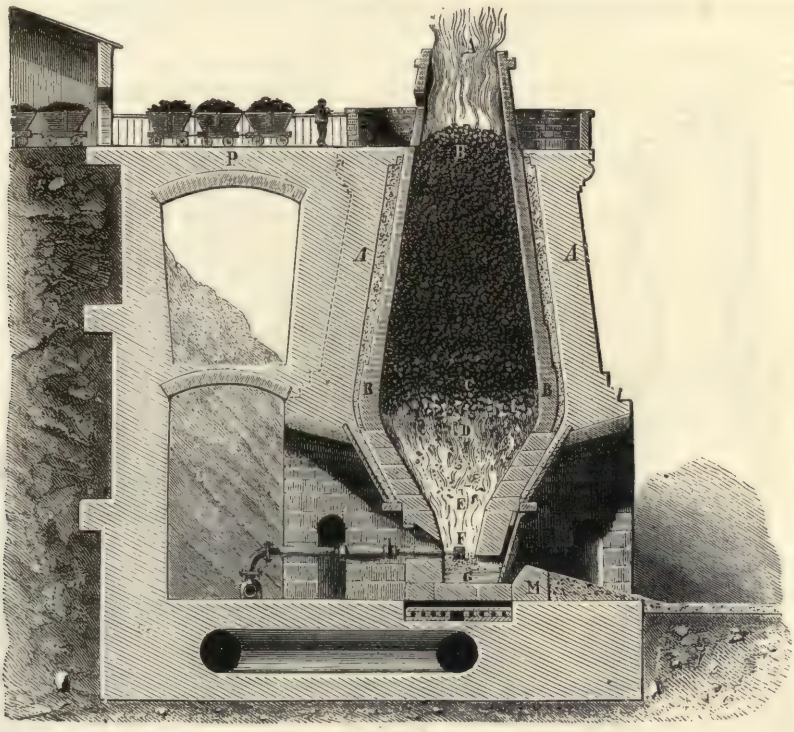
In ancient times, and to a small extent even yet in some districts, a direct preparation of iron from its ores was very general. In this manner very pure and tough bar-iron was obtained, but the process admitted only of a limited extension, and the ores were imperfectly utilised.

The ores are roasted in heaps or in special kilns, in order to expel carbonic acid and water, to make the mass more brittle and porous, and thus more susceptible to reduction, and to convert any ferrous oxide present into the ferric state, so as to be less readily convertible into slag. The ores, roasted or raw, are, if necessary, broken up by means of stamps, rollers, or special crushing machines (such as Blake's ore-breaker); the richer ores are mixed with lower qualities (assorted) in proportions which, according to experience, yield the best returns. The coal acts in smelting as a source of heat and (*per se* as well as in the state of carbon monoxide and dioxide) as a reducing agent. In order to unite the reduced iron into a mass before smelting, materials are added which combine with the gangue to form a readily fusible *slag*. This slag serves for removing foreign matter, partly injurious to the quality of the iron, by facilitating the coalescence of the reduced metallic particles, and by protecting the crude iron already formed from the oxidising action of the blast. If silica is deficient, sand or quartz is added; if bases are wanting, limestone or fluor-spar is supplied. The charge as introduced into the furnace should not contain more than 50 per cent. of iron.

The smelting process is almost exclusively executed in so-called blast furnaces. A blast furnace is a round shaft-oven (Fig. 126), surrounded with a strong wall, *A*; it is 15 to 30 metres in height, the inner part of which has the shape of two truncated cones fixed to each other at their bases. The wall of the shaft, *B*, is enclosed by a second, *A*, which joins up to the massive brickwork of the furnace. Between the two there is left a space, which is filled up with a bad conductor of heat, such as ashes, and which gives the necessary play-room for the expansion of the inner shaft by heat. The part from *B* to *C* is the *shaft;* that from D to E, the *boshes;* the part *B*, where the diameter is greatest, is the *belly* or upper part of the boshes. Below the boshes the

space contracts to F, the crucible or hearth. Here the smelting process takes place, and here are, opposite to each other, apertures with conical tubes into which enter the mouth-pieces or *tuyères* of the pipes which supply the furnace with air. The open top or mouth of the furnace, *A*, serves for introducing the charge. Such furnaces were formerly built on a declivity, so that fuel and ore, &c., could be conveyed to the mouth on a sloping road, or it was brought over the bridge P. The lower part of the hearth is prolonged towards the front, forming the hearth-pan or fore-hearth, which is enclosed by the dam-stone, M. This stone stands off a little from the wall and forms a slit,

Fig. 126.



the so-called tap-hole, which is stopped with clay during smelting, and serves afterwards to discharge the molten metal and the slag.

Latterly, the furnaces are no longer built so massive. The bridge, *w* (Fig. 127), leading to the top, and the upper wall of the furnace rest upon iron pillars. The hot blast is introduced through a ring-shaped pipe, *r*, lying round the furnace through tuyeres cooled by water. The furnace mouth is provided with a moveable cover; ore, coke, etc., are thrown into the funnel, *e*; the cover is then raised for a moment to let the charge slide down into the furnace, and it is then immediately closed, so that the gases are compelled to pass through the top-piece, *g*, and the connecting pipes, to the apparatus for heating the air, or to the boiler fires.

Air-Heating.—One of the most important modern improvements has been the use of the hot blast. The influence of the raised temperature of the air upon the consumption of fuel and the performance of the furnace is shown in the following table. The addition of purple ore served for closing the joints of the funnel:—

Weekly Production. metric tons.	Heat of Blast.	Charge per Ton of Crude Iron.				Silicon per Cent. in Crude Iron.
		Coke. kilos.	Limestone. kilos.	Roasted Ore. kilos.	Purple Ore. kilos.	
406	532	1209	584	2398	18	2·4
415	631	1179	584	2408	18	2·6
456	702	1169	616	2408	18	2·5
568	722	1157	618	2400	18	2·5
465	760	1132	620	2388	18	2·6

The heating apparatus may consist either of a single chamber built of stone, serving both for air and heating gas, and which works alternately and with interruptions, or

Fig. 127.

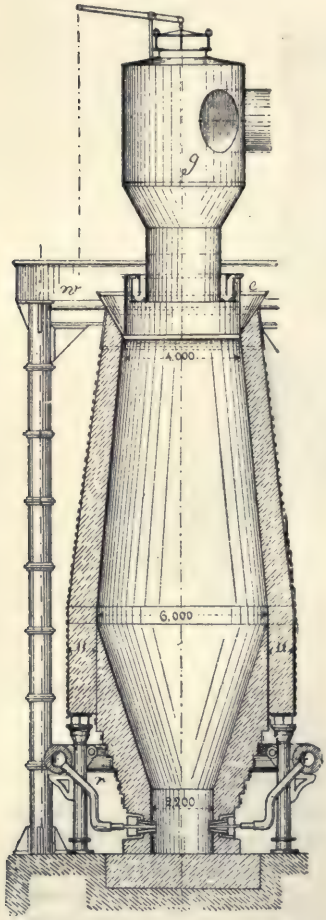


Fig. 128.

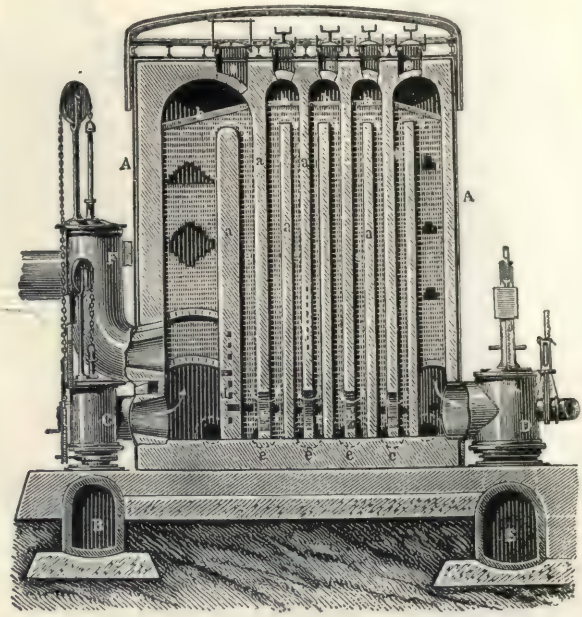


Fig. 129.

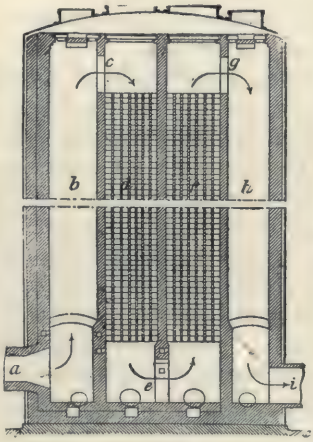
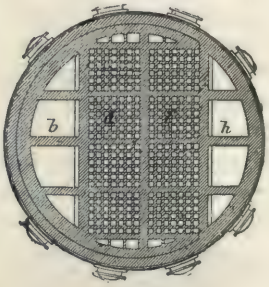


Fig. 130.



it may comprise two iron chambers working continuously. The stone apparatus bears a higher temperature, but requires a larger heating surface in order that the variation of temperature on changing may be the smaller. Hence, they are more expensive to erect, but cheaper to maintain, though they require trustworthy attendants during the change. In the iron apparatus,

the temperature of the air is limited (up to the point at which cast-iron softens), the heating surfaces and the cost of erection are smaller; the maintenance is more costly, though the cleaning is easier.

The air-heater of Whitwell consists of a sheet-iron cylinder A (Fig. 128), lined with fire-stone and fitted with partitions, a. The furnace gases led in through B pass through the valve-box, C, into the first chamber, where they burn along with air which is introduced simultaneously, and pass in the direction of the arrows through the apertures, b, and the valve-box, D, to the flue, E. If the stone lining is sufficiently heated the connection with B and E is closed, and blast-air is driven in, which takes up the heat stored in the stones, and passes through F into the furnace. The top and the floor are provided with apertures, e e, for cleaning.

In Macco's heater, the furnace gases pass through the flue, *a* (Figs. 129 and 130), pass upwards in the chamber, *b*, of the apparatus, enter the grated chamber, *b*, passing downwards, and unite again in the lower chamber, *e*. Hence the gases pass into the second grated compartment, *f*, in which they move upwards, arriving through the aperture, *g*, into the last compartment of the apparatus, turning downwards and escaping through the chimney, at *i*. Both immediately after entering the apparatus at the lower part of compartment, *b*, and in the lower middle compartment, *e*, heated air is conveyed to the gases for their more complete combustion. The air to be heated takes the opposite direction. By the use of the intermediate chambers, *d* and *f*, a large heating surface is supplied and the air is raised to a high temperature.

The Smelting Process.—The furnace is heated first by kindling wood on the hearth and then introducing the fuel (generally coke, sometimes anthracite, rarely crude coal) until the entire shaft is filled with ignited matter. At the same time, the blast is turned on and ore and fuel are introduced in successive layers. As the fuel burns, and the ore and fluxes, &c., melt, the layers sink gradually down. The silica melts with the earths and oxides, forming slag, whilst the reduced semi-liquid iron unites with carbon to form an easily fusible crude iron. The melted iron collects at the bottom of the hearth, and upon it floats the slag, which is let flow off. The liquid iron is from time to time run off by opening the tap-hole, and conveyed to the moulds through a channel prepared in the sand in front of the furnace. During tapping, the blast is stopped.

Heat-conditions of the Blast Furnace.—According to Lürman, we must not think of the heat as being distributed in successive zones of the blast furnace. The charges tend towards the axis of the melting column, and the gases to the circumference, so that here the reactions take place more rapidly than in the middle. Heat is consumed—

(1) For the *evaporation of water* and for the escaping gases. Samples of gas are to be taken where they are in a state of mixture. For the evaporated water it is not sufficient to calculate 637 heat-units, but—

$$\text{Heat} = 606{\cdot}5 + 0{\cdot}305\,(100) + 0{\cdot}48\,(t - 100).$$

For the remaining gases the calculation is carried out in the usual manner. As to the quantity of dust thrown off at the top, there are few trustworthy statements. Independently of the character of the ores, the quantity of dust will depend on the rapidity of the charges and the temperature of the furnace. At any rate, the escape of dust is a cause of the expenditure of heat and the loss of material which must be taken into account. No great error will be committed if we take as specific heat the figure which has been established for porous refractory stones and fire-bricks (about $= 0{\cdot}22$), and multiply it by the temperature of the gas and the quantity of dust. For 5 per cent. of dust, or 50 kilos. per ton, and 100° as the temperature of the gas, the quantity of heat would be $50 \times 400 \times 0{\cdot}22 = 4400$ heat-units per ton yield of crude iron.

For hotter working, 10 per cent. of dust, and a gas temperature of 600°, we have $100 \times 600 \times 0{\cdot}22 = 13{,}200$ heat-units.

(2) The liberation of carbonic acid from the carbonates of the ores and the additions has a great influence on the entire character of the blast-furnace process. It absorbs a very considerable quantity of heat, and the course of its evolution extends over a great space in the furnace shaft. Where there are very abundant additions of limestone, the liberation of carbonic acid extends down to the region of the smelting (strictly speaking), and perhaps the last traces of the volatile constituent of the carbonates is expelled only by the silica, which is already active in the formation of slag. It is decided that the expulsion of carbonic acid in the blast furnace, though it probably begins at 800°, requires for its completion about 1700°, whence the final decomposition of the carbonates takes place in the zone of the most dazzling white heat.

(3) *Processes of Reduction.*—The most important compound of iron is the magnetic oxide, Fe_3O_4. Here there must be utilised a reduction-heat of only 1648 heat-units, instead of the mean value of 1887 heat-units proposed by Grüner for iron oxide; the expenditure of heat per iron unit is certainly smaller. The decomposition heat of iron carbonate, when split up into carbon dioxide, and ferrous oxide (half of which has to be further oxidised to ferric oxide) has not been measured. Dürre takes in its place the heat of calcium carbonate. The silicate is more important, as considerable portions of slags undergo refining. For the combination-heat of ferrous oxide and silica there are no accurate determinations. According to Tholander, 310 heat-units would be calculated as the combination-heat of ferrous oxide and silica. For 1 kilo. of crude iron, containing 95·5 per cent. Fe, there would then be $0{\cdot}955 \times 310$ or 296·1 heat-units used in the decomposition of silicate, besides the reduction-heat of the liberated ferrous oxide (according to Favre and Silbermann, = 1352 heat-units). We see that the sum 1352 heat-units + 296·1 heat-units = 1648·1 heat-units coincide almost exactly with the reduction heat of magnetic oxide, 1648 heat-units, whence we should conclude that a pure ferrous silicate and the magnetic oxide are almost equally reducible if Tholander's supposition is correct, and there remained on the reduction of ferrous silicate, metallic iron and free silica. It is only, however, reduced to a small extent, whilst most of it passes into the slag. Ferrous silicate is usually considered difficult to reduce, though easily fusible, and, as it generally holds in solution variable quantities of magnetic oxide, its reductibility cannot be pronounced great. For the manganese compounds we may provisionally assume for $Mn_3O_4 = {}^{11}/_{8} \times 1648 = 2264$ heat-units; for Mn_2O_3 ${}^{11}/_{8} \times 1887 = 2595$ heat-units; for sulphur from sulphur acids 3226 heat-units; for phosphorus from phosphoric acid (P_2O_5) 5747; from $H_3PO_4 = 9662$ heat-units. Whether the lower value is accurate must remain a question, and only the circumstance that also the combination-heat of iron phosphide, as well as the heat evolved by the combination of lime and magnesia with the slag cannot be determined, causes the proposal to use 5747 instead of 9662 heat-units to appear less questionable.

The heat capacity of the reduction products is known only in part, and it is hence difficult to form a correct conception of the temperature at which phosphoric acid is reduced. In any case, this reduction occurs at so high a temperature that it takes place on the hearth of the furnace and in presence of solid carbon. Carbon monoxide can scarcely be active here; at least, laboratory experiments show that the phosphates cannot be reduced by a current of carbon monoxide alone. How far the liquefied iron in the blast furnace participates in the reduction of the phosphoric acid is hard to say.

Experiments in the refining process show that the prolonged contact of metallic iron and phosphatic slags reduces the phosphoric iron contained in the latter to phosphorus. On the other hand, the first experiments with the Thomas and Gilchrist process have shown that dephosphorised iron covered with a phosphatic slag can take up phosphorus again on treatment with highly carburetted iron (spiegel-eisen and

ferromanganese), which can only have been isolated by the transit of carbon monoxide through the layer of slag or in consequence of the action of the same compound upon finely divided iron-phosphates in the liquid iron. All these processes, if further studied, may lead to important conclusions on the behaviour of phosphoric acid in the blast furnace. Arsenic acid scarcely comes into question.

Of especial importance is *silica*. As soon as from any cause a very infusible slag is formed, or is intended to be formed, there is seen in the crude iron a separation of graphite regularly preceded by the taking up of silicon. The medium for the reduction of silicon is partly the silica in the slag, partly that of the furnace walls, though these first yield silica for reduction. According to experiments on the reductibility of iron ores, we must assume that a charge free from slag, *i.e.*, without the addition of puddling slags, as it is generally made up from brown iron ore, hæmatite and roasted iron-spar for the production of Bessemer iron is chiefly reduced in the shaft, and that by means of carbon monoxide, whilst a charge containing a large proportion of slags is reduced only on the hearth in the state of complete fusion.

The nature of the slags is here nearly indifferent, since both in acid and in basic slags, in those where calcium silicates, and in those where aluminates predominate, the iron takes up silicon and liberates carbon as soon as the temperature is high enough. The reduction-heat with the combustion-heat of silicon may be estimated at 7830 heat-units, referred to the silicon of crude iron. The reduction-heat of the earths and the alkalies does not come under notice.

(4) *Melting-heat of Crude Iron.*—Grüner has proposed mean values for practical utilisation, to be applied when direct calorimetric determinations have not been simultaneously made on the iron, the slag, the hot blast and the escaping gases. These mean values are: 300 heat-units for grey cast iron, 275 for white cast iron, 25 of which may be considered as latent in the grey and 35 in the white iron.

(5) *Melting-heat of Slags.*—The most comprehensive experiments have been made by Akermann. For blast furnace slags he found 340–410 heat-units. The quantity of heat ascertained at the furnace itself will always be greater than that found in an unmelted slag, for in addition to the true melting-heat, the slag flowing out of the furnace contains the sum of the heats of combination and decomposition, whilst in measuring the heat in an unmelted slag, the mere melting-heat alone comes in question. In slags worked for grey cast-iron we may assume 500 heat-units, and in those for white iron 450 heat-units.

(6) *Decomposition of the Atmospheric Moisture.*—Grüner in his calculations assumed an atmospheric moisture of at least 0·0062 in his calculations. The influence of foggy or wet weather, both upon the course of the process and the results, is sufficiently known to every practical man, and shows that attention to the moisture of the air is justifiable.

(7) *Water and Air used for Refrigeration.*—Some observers have attempted to determine the quantities of heat which have been transmitted to the water and the air used for refrigeration.

(8) *Losses* include all the heat expended upon the furnace itself. They can be found only in and by subtracting all the known and determinable expenditures of heat from the total heat produced, and in spite of repeated experiments they have not been determined with certainty. There occurs in the first place a transfer of heat from the interior of the furnace to the substance of the walls, which, in the layers next to the interior, have almost the same temperature as the adjacent zone of the furnace. A part of the heat is conveyed through the entire thickness of the walls according to their conductivity, the size of the surface, &c., to the outer surface of the walls and thence to the ambient air, partly by radiation and partly by conduction. This quantity of heat can scarcely be regarded as total loss, since the interior of the furnace must of necessity have the temperature of the process going on within.

The consumption of fuel in the working of the blast-furnace depends essentially on the reducibility of the ores. The experiments of Akermann and Sarnstrom prove that ferric oxide is reduced by carbon monoxide to magnetite. Already, at 450° the carbon monoxide may already contain 20 per cent. of carbon dioxide and still has a reductive action upon the oxides; at 900° the oxide loses oxygen even in carbonic acid free from carbon monoxide. In order to deoxidise magnetite at 850°, the gas must not contain more than 3 vols. of carbon dioxide, and if the reaction is to be effected at 300° to 350°, the carbonic acid must not exceed 2 parts. To produce ferrous oxide, not more than 0·5 part of carbonic acid must be present to 1 part of carbon monoxide.

Hence, the smallest consumption of fuel for a blast-furnace may be calculated if it is possible to effect the reduction of the ore with carbon monoxide exclusively.

According to the formula, $3CO + FeO = 2CO + CO_2 + Fe$, for each mol. of iron there must be present at least 3 mols. of carbon monoxide. If the ore higher up in the furnace is in the stage of oxidation of magnetite, then, according to the formula, $9CO + Fe_3O_4 = 5CO + 4CO_2 + 3Fe$, five parts carbon monoxide must be accompanied at most by 4 parts of carbonic acid, whilst the same 5 parts of carbon monoxide, as far as the reduction of magnetite is concerned, may be accompanied by at least 10 parts of carbonic acid. If the ore consisted at first of oxide, the equation $3CO + Fe_2O_3 = 3CO_2 + 2Fe$ signifies that the escaping gases, if the final reaction with carbon monoxide is to be produced, must contain at least equal volumes of carbon monoxide and carbonic acid, whilst oxide can be reduced to magnetite even with a gaseous mixture containing 20 parts of carbonic acid. Hence, it follows that the difficulties of reduction grow enormously with the decreasing grades of oxidation of the iron, and that the final reduction of ferrous oxide requires much more carbon monoxide than is necessary for the partial reduction of the higher grades of oxidation. For the mere reduction of the ore by means of carbon monoxide, there must be burnt by the blast at least $3C : Fe = 0{\cdot}643$ kilo. carbon. If we further consider the 4 per cent. of carbon taken up by the raw iron, we have 0·657 carbon. If the ore was pure magnetite, then for each kilo. of non-volatile carbon we should have at most—

$$(3 \times 56 + 4 \times 16) : [(9 \times 12) \times (3 \times 12 + 0{\cdot}04 \times 56) : (3 \times 12)] = 2{\cdot}03 \text{ kilos.}$$

of pure magnetite; then percentage of the escaping gases in carbonic acid and carbon monoxide would be in volume 0·80 and in weight 1·26. If the ore was pure oxide, we should have—

$$(2 \times 56 + 3 \times 16) : [(6 \times 12) \times (3 \times 12 + 0{\cdot}04 \times 56) : (3 \times 12)] = 2{\cdot}10 \text{ kilos.}$$

oxide, and the mixture of gas would be 1·00 or 1·57.

If the reduction is thus to be effected by carbon monoxide alone, there must be burnt with the air of the blast at least 64·3 kilos. of carbon to 100 kilos. of reduced iron. But, contrary to expectation, this quantity in blast-furnaces is often smaller, whilst the gases are not richer in oxide. Hence, it follows that the reduction is effected not only by carbon monoxide, but also by carbon. The fear of loss of heat in the carbon-reduction as compared with the oxide-reduction has been the cause that the consumption of coal is now in that case less than it ever could have been in oxide reduction. The lost heat is substituted by hotter air from the blast, whereby the crude iron is rendered again poorer in carbon and richer also in silicon by overheating in the moulds.

The consumption of fuel can scarcely be reduced lower in many cases. Fuel could be further economised only by very hot air from the blast, with a simultaneous introduction of carbon monoxide; but this gas would have to be produced more cheaply than in the blast furnace itself. The oxide gas must thereby not be mixed with hydrogen, as Bell proposes, since this chiefly promotes reduction by carbon, to which the supply of oxide gas would act antagonistically.

The following calculation shows the average heat required for smelting crude iron in charcoal furnaces. For comparison there are also given the corresponding values which express the consumption of heat in smelting 100 kilos. of coke iron :—

Consumption of Heat for—	Swedish Charcoal Furnaces. heat-units.	Cleveland Coke Furnaces. heat-units.
Evaporation of moisture of fuel	8,155	1,620
Reduction of iron from ore	158,805	165,540
Saturation of reduced iron with carbon	9,600	7,200
Expulsion of carbonic acid from limestone	7,105	20,065
Its decomposition by carbon	7,360	20,800
Decomposition of moisture of air	6,800	12,200
„ of phosphoric acid and silica	2,610	20,870
Fusing crude iron	33,000	33,000
„ slag	41,350	72,600
Heat escaping through masonry, estimated	12,715	18,290
Absorption by refrigerating water	5,545	9,090
Escape of heat in gases at mouth	34,565	37,710
Total heat-units required	327,610	419,005
Heat evolved, calculated according to composition, weight, and temperature of fuel of escaping gases and of air	318,175	423,860

Hence fully 30 per cent. more heat is required for smelting Cleveland irons than for the richer hæmatites and magnetites of Sweden. The consumption of materials for 100 kilos. crude iron was as follows :—

	Sweden.	Cleveland.
Fuel	97·4 kilos.	102·0 kilos.
Limestone	19·2 „	46.9 „
Ore	197·8 „	234·7 „
Temperature of blast	211°	563°
„ of escaping gases	289	262

It is known that the ore is the source of the oxygen which converts carbon monoxide into carbon dioxide. In addition to the carbon dioxide thus formed, a certain quantity is contributed by the limestone, and a further portion by the dissociation of the carbon monoxide, since two equivalents of this gas are resolved into carbon dioxide and carbon within the pores of the ore undergoing reduction. But as soon as the carbonic acid exceeds a certain proportion, there sets in—the temperature and other circumstances permitting—an opposite reaction: carbonic oxide is formed by the carbon of the fuel.

The gases of the Cleveland blast furnaces, those especially of 23 to 24 metres in height, are notable for the small quantity of carbonic acid contained in them below a certain depth. The following examples illustrate this proposition for a furnace of the capacity of 496 cubic metres—

Beneath the Mouth.	No. I.		No. II.	
	CO_2.	CO.	CO_2.	CO.
5 metres	2·22	34·08	2·25	33·31
6 „	0·67	35·11	0·73	34·84
12 „	1·09	34·96	1·00	35·08
16 „	1·51	35·24		
20 „	0·50	35·92	0·49	36·03
21·5 „	0·00	36·63	0·00	37·60
At the tuyeres	0·81	37·70	0·73	37·86

A charcoal blast furnace of 15·95 metres in height and 101 cubic metres capacity gave, in the average of two determinations—

	CO_2.		CO.
3·4 metres below mouth	16·39	...	13·11
5·2 „ „	17·80	...	10·89
7·0 „ „	9·60	...	21·59
8·2 „ „	2·68	...	30·66
10·4 „ „	11·60	...	20·06

Various samples of flue dust had the following composition :—

	KO.	NaO.	CaO.	MgO.	Fe_2O_3.	MnO.	ZnO.	PbO.	SiO_2.	Al_2O_3.	S.	ZnS.
Gleiwitz . .	12·28	12·58	6·15	5·87	9·50	0·31	25·51	13·73	17·72	3·94	0·24	—
Tarnowitz . .	—	—	—	—	—	—	35·65	10·64	15·55	4·21	—	—
? . .	17·05	9·53	25·95	2·31	0·91	0·37	1·30	—	24·05	10·90	1·71	—
Cleveland . .	—	4·70	12·30	5·03	14·22	—	10·48	—	22·60	8.20	0·17	13·70

The proportion of cyanogen compounds in the gases and the dust deserves notice. According to the views of Berthelot, there is first formed in the blast furnace potassium acetylide, C_2K_2, which then combines directly with nitrogen to potassium cyanide, 2(CNK). How considerable may be the production of metallic cyanides in blast furnaces worked with coal appears from an investigation by Bunsen and Playfair on the English manufacture of crude iron, according to which 112·5 kilos. of potassium cyanide were produced daily in a blast furnace. According to Bell, the following quantities of potassium and sodium were found in combination with carbon dioxide, oxygen, or cyanogen in 1 cubic metre of the gases of a Cleveland coke-blast furnace of 495 cubic metres capacity, and a height of 24·4 metres. The gases were drawn on six successive days at the height of 2·44 metres above the hearth :—

	I.	II.	III.	IV.	V.	VI.	Average.
Potassium and sodium .	46·49	30·17	33·15	21·09	31·65	11.83	29.11 gramme
Cyanogen	19·00	12·93	17·32	11·34	20·61	9·16	15·06 „

On the same days the escaping gases contained :—

Potassium and sodium .	12·20	15·30	6·68	5·89	4·29	—	9·07 „
Cyanogen	4·00	6·60	3·57	2·91	1·79	—	3·77 „

Slags.—The composition of the slag is, to an experienced eye, an important indication of the working of the furnace. The composition is, of course, widely different—*e.g.* :—

	Mariazell (Styria).	Scotch.	
		Granular.	Vitreous.
Silica	43·850	57·95	52·71
Alumina	4·650	21·96	21·44
Manganous oxide	2·610	0.37	0·64
Ferrous oxide	0·540	0·05	0·36
Baryta	0·850		
Lime	23·300	16·24	19·13
Magnesia	22·700	0·43	3·70
Potash	0·480		
Soda	0·050		
Calcium sulphide	1·010	3·00	2·02
Phosphoric acid	0·009		

The crude grey iron from Mariazell, in Styria, belonging to the first slag contained :—

Carbon	0·354
Graphite	2·837
Silicon	2·953
Sulphur	0·018
Phosphorus	0·045
Copper	0·220
Cobalt and nickel	0·013
Manganese	2.980

The blast furnace works of Ougrée exhibited at Antwerp the following analyses of slags, together with the accompanying kinds of iron :—

Crude Irons.	White Iron.	Spiegel.	Spiegel Bessemer.	Semi-Bessemer.	Bessemer.	Bessemer, Extra.	Thomas.	Crude Iron for Castings.
	—	—	Grey, Coarse, with Spiegel.	Spiegel Fine Grain.	Nucleus Coarse, Exterior Fine.	Great Separation of Graphite.	Radiating to Specular, Grey Points.	Strong Grey.
Carbon . . .	4·400	5·800	5·100	4·000	4·500	4·500	4·325	3·987
Silicon . . .	0·409	0·503	1·127	1·121	2·463	2·845	0·807	1·307
Manganese . .	0·131	7·232	4·213	2·988	2·042	0·9–0·4	1·820	0·407
Sulphur . . .	0·329	0·000	trace	trace	0·014	0·010	0·054	0·056
Phosphorus . .	1·528	0·892	0·223	0·093	0·060	0·048	2·344 ?	0·157

Slags.	Dark Brown, Firm.	Light Green.	Light Grey, Firm.	Light Grey.	Light Crumbling.	Crumbling.	—	Chiefly Crumbling.
Silicon . . .	34·35	32·25	33·10	34·00	32·21	30·00	32·97	35·50
Alumina . . .	14·66	11·17	10·33	9·79	11·57	12·34	12·44	8·72
Lime	42·66	46·20	49·70	47·00	50·42	51·00	47·95	46·50
Magnesia . . .	2·00	2·02	1·34	3·30	1·37	2·34	1·37	3·20
Manganous oxide .	0·92	5·07	2·04	2·32	0·85	0·30	2·26	1·58
Ferrous oxide . .	3·30	0·60	0·67	0·65	0·76	1·05	1·47	1·16
Sulphur . . .	1·42	2·52	2·69	1·80	2·72	2·73	1·42	1·64
Phosphorus . .	0·14	0·02	0·03	0·01	0·01	0·02	0·08	0·02

Blast furnace slags are used for the preparation of artificial stone, for road-making, as a material for cement, for bottle-glass, for enamelling, for manures.* Slags, if not basic, are also used for the manufacture of aluminous products.†

Crude Iron.—The iron run off from the blast furnace contains carbon (both free, as graphite, and in combination, as iron carbide), silicon, sulphur, phosphorus, manganese, &c. According to the nature of the carbon, it is distinguished as white and grey crude iron.

The white iron is distinguished by its silvery white colour, hardness, brittleness, brightness, and high specific gravity (7·58 to 7·68). Its carbon is in a state of chemical combination. Sometimes it displays prisms, and is then known as spiegel-eisen, which is obtained from manganiferous iron spar. It may contain from 4 to 15 per cent. of manganese. In the production of steel from such spiegel-eisen the manganese protects the carbon against too rapid combustion.

Grey crude iron varies in colour from a light grey to a deep blackish grey, and is of a granular or scaly texture. It is softer than white iron and more fusible. It contains much graphite and little carbon in chemical combination. It is used for castings, as it fills the moulds more sharply and cleanly than white iron, which hardens with blunt extremities and a concave surface. White (especially manganiferous) crude iron is particularly suited for the preparation of bar iron and steel (Bessemer steel).

The character of crude iron depends not merely on the charge, but on the temperature of the furnace and the way of working. White iron seems to be first formed in the furnace, and to pass into grey iron at a very high temperature. If ore additions (fluxes, &c.) and fuel are duly proportioned, the product is chiefly white iron, and the slag is never dark. If the fuel is deficient, much ferrous oxide passes into the slag, and gives it a dark colour. If there is an excess of fuel, grey iron is produced.

* This use is practicable only with the basic slags of the Thomas and Gilchrist process, which are very rich in phosphates.

† *E.g.*, crude aluminium chloride for the treatment of sewage. See J. W. Slater's process, patent No. 12,830, A.D. 1884. It has been proposed to make bricks of slag, but houses, &c., built of such material never become dry, as there is no interchange of air through the walls.

(2) Examination of Iron and Steel.

The most important points to be determined are the quantities of carbon, silicon, phosphorus, sulphur, manganese; secondarily, those of tungsten and titanium. The microscopic examination is acquiring importance.*

In determining total carbon in iron according to Wöhler's process (heating the sample in a current of chlorine, and burning the residue for converting the carbon into carbon dioxide), we obtain, according to Gintl, defective values, as it is not possible by ordinary means to obtain a current of chlorine absolutely free from oxygen, perhaps in consequence of the formation of oxides of chlorine obtained during the action of hydrochloric acid upon manganese peroxide. This error is avoided by passing the current of chlorine (freed from hydrochloric acid and watery vapour by washing and careful drying) over a stratum of fragments of charcoal of about the size of lentils, about 10 centimetres in length, and kept at a red heat. The charcoal must have been previously ignited in chlorine. The gas so purified is then allowed to act upon the iron, which must be used as borings. Ullgren oxidises the carbon by means of chromic acid, and weighs the carbonic acid produced; Wiborgh determines it volumetrically.

For determining the carbon present as graphite the sample is generally dissolved in dilute hydrochloric acid in the absence of air, when the residual carbon is washed out and weighed. The combined carbon appears as a residue. Eggertz determines combined carbon by dissolving the sample in nitric acid and comparing the solution with known standards. The process is adapted for checking work.

For determining sulphur the sample is dissolved in nitric acid, and the sulphuric acid formed is precipitated with barium chloride. Less accurate are the processes in which the sample is dissolved in hydrochloric acid; the sulphur being driven off as hydrogen sulphide and conducted into metallic solutions.

For determining silicon 5 grammes of the sample are dissolved in nitric acid or bromiferous hydrochloric acid, or in sulphuric acid with potassium chlorate; it is then evaporated to dryness, moistened with hydrochloric acid, dissolved, and the silica is filtered off.

For determining phosphorus the sample is dissolved in nitric acid, evaporated to dryness, slightly ignited, re-dissolved; the phosphoric acid is precipitated with molybdic acid, the precipitate dissolved in ammonia and reprecipitated with magnesia mixture.

The following analyses of crude iron may be appended :—

——	I.	II.	III.	——	IV.	V.
Graphite	2·171	3·156	6·05	Carbon	4·323	4·166
Combined carbon	0·086	1·347		Sulphur	0·014	0·035
Phosphorus	0·459	0·842	6·37	Phosphorus	0·059	0·090
Sulphur	0·036	1·267	0·06	Silicon	0·997	0·584
Silicon	3·265	2·721	2·41	Manganese	10·707	5·920
Manganese	0·388	2·401	6·28	Cobalt	trace	trace
Aluminium	0·028	—	0·08	Nickel	0·016	„
Chrome	0·027			Zinc		
Vanadium	0·012			Copper	0·066	0·046
Copper	0·009			Lead		
Arsenic	0·015			Potassium	0·063	
Antimony	0·011			Aluminium	0·077	0·068
Cobalt and nickel	0·035			Calcium	0·091	trace
Zinc	trace			Magnesium	0·045	0·058
Calcium	0·072	—	0·46	Titanium	0.006	
Magnesium	0·100	—	0·25	Arsenic	0·007	0·032
Titanium	0·024			Antimony	0·004	0·026
				Tin	—	
				Nitrogen	0·014	
				Oxygen (in slag)	0·665	

* See *Select Methods*, by W. Crookes, F.R.S., pp. 145–195.

I. is a black crude iron, according to Fresenius; II. is a very grey crude iron from Gartsherrie; III. grey crude iron from bog-ore at Helbo (charcoal); IV. Spiegel iron from Lohe, according to Fresenius; V. Spiegel-eisen from St. Louis.

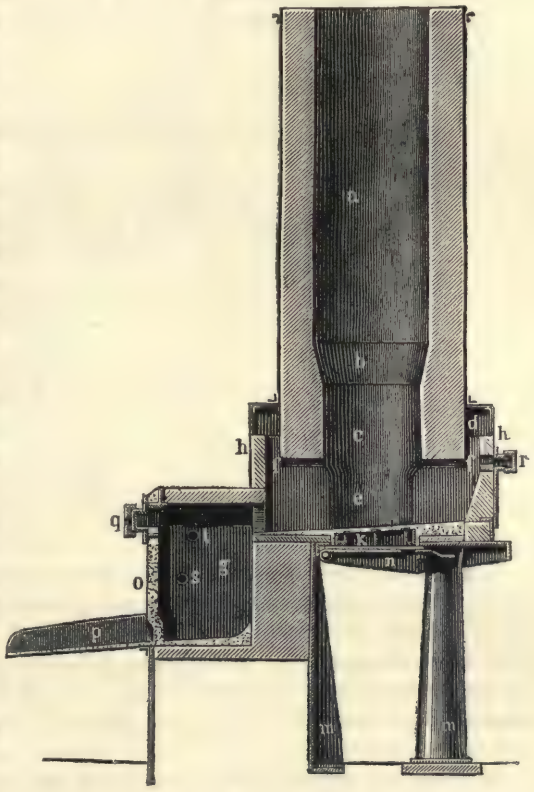
The analysis of Gleiwitz coke iron has given the following results:—

	C.	Si.	S.	P.	Mn.
Spiegel, crude	3·35	0·317	0·030	1·29	3·60
White	5·49	0·800	0·010	0·28	3·73
Finely granular	3·20	1·210	0·114	0·81	1·70
Coarse „	4·38	2·020	0·118	0·90	1·65

(3) Iron Founding.

Although iron can be cast direct from the blast-furnace it is generally preferred to re-melt the pigs; this is effected either in crucibles in shaft- or cupola-furnaces, or in reverberatories. The cupola-furnaces are by far the most generally used, the preference being given in Germany to the design proposed by Krigar. The cylindrical shaft, a (Fig. 131), has a short chamber, b; the compressed air issues from the ring-shaped channel, d, through slits, f, into the melting-box, c, e. The melted iron collects in the fore-hearth, g, from which the slag can flow off at s or t. The door, o, lined with fire-clay, is provided with an aperture above the out-flow channel, p. At q there is an eye-hole, and at r an opening for cleaning the slits. The lower part of the furnace is, with the sheet-metal screen, h, and stands on the ribbed cast-iron plate, k, which lies on the iron pillars, m. When the melt is complete, the last residues are removed through the trap door, n. In the cupola-furnaces of Greiner and Erpf the air enters through different rows of tuyères to burn the carbon monoxide.

Fig. 131.



The author found on examining Krigar furnaces that the ratio CO_2: CO in the escaping gases is now 2 to 3, whilst it was formerly about 0·8; the consumption of coke per 100 kilos. iron is now reduced from 20 to 6 kilos. The sulphur escapes partly in the gases, and in part, if sufficient lime is present, it enters the slags, as the following analyses show:—

——	Slags from Former Times.	Slags from Hannoverian Cupolas.			From Spiegel.	Slags from Irons for Basic Process.		
SiO_2	60·05	56·04	55·01	50·48	36·56	37·05	42·08	52·96
Al_2O_3	18·00	11·55	11·61	10·68	11·57	11·08	10·81	12·80
Fe_2O_3	—	—	—	—	—	—	0·85	1·25
FeO	4·61	15·34	14·91	20·98	0·78	1·59	6·28	4·36
MnO	8·29	4·02	1·06	4·01	19·80	14·09	5·66	4·31
CaO	6·29	9·74	15·05	9·85	28·97	29·64	29·50	19·63
MgO	0·25	0·51	0·49	0·84	1·92	20·79	3·65	2·12
Ca	0·41	0·21	0·28	0·22	—	1·98	—	0·47
S	0·33	0·17	0·22	0·18	0·40	1·58	0·48	
P_2O_5	—	—	—	—	0·04	0·10	1·00	0·11
SO_3	—	—	—	—	0·05	—	0·04	0·40

The iron present in the cupola slag is derived partly from the ash and partly from the crude iron; the latter is the more strongly oxidised the less carbon monoxide is formed, as shown, *e.g.*, in the slags of the Hannover cupolas. The richer the crude iron is in manganese the more both the iron and the silicon are protected from oxidation.

The changes which iron undergoes on re-melting in the cupola were examined by Ledebur :—

——	C.	Si.	Mn.	Cu.	P.
Pig	4·173	1·528	2·084	0·079	0·331
After 1st smelting	3·586	1·447	1·599	0·150	
„ 2nd „	3·860	1·370	1·399	0·080	
„ 3rd „	3·763	1·378	1·038	0·079	
„ 4th „	3·686	1·334	0·736	0·079	0·475

On melting pig-iron with lime and fluor-spar Rollet obtained :—

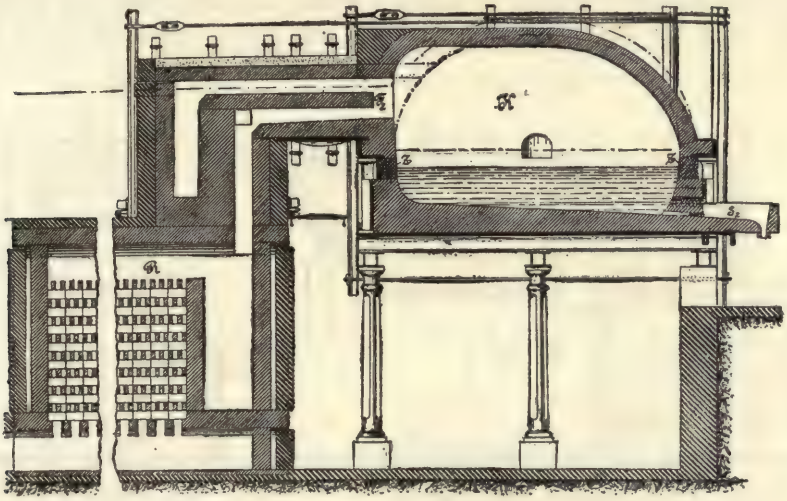
——	I.		II.		III.	
	Before Smelting.	After Smelting.	Before Smelting.	After Smelting.	Before Smelting.	After Smelting.
Ca	3·500	3·500	2·900	3·088	2·550	2·800
Si	0·900	0·380	0·655	0·060	0·450	0·120
Mn	1·300	0·815	traces	traces	traces	traces
S	0·220	0·015	0·375	0·015	0·520	0·040
P.	0·070	0·058	0·350	0·068	1·950	0·415

Good casting-iron should contain as much carbon as possible, in the form of graphite, and be consequently very coarse in grain (generally 3 to 3·5 per cent.); the manganese should be low, not exceeding 0·75 per cent. A high proportion of silicon—at least 2 per cent.—is, according to Schmidt, indispensable. A low proportion of phosphorus is advantageous, and 1 per cent. is the utmost limit. For castings which must have great absolute strength the margin lies at 0·5 per cent. Sulphur must not exceed 0·06 at the outside.

Melting in a reverberatory furnace has the advantage that the iron does not come in contact with the coke or its ashes, and is consequently less modified than in the cupola. On account of the high temperature required, only furnaces with a storage for heat can be advantageous. The reverberatory designed by Fr. Siemens has a round chamber *K* (Figs. 132 and 133), with a vault as shown by dotted lines. To the furnace chamber there are joined two pairs of gas and air flues, F_1 and F_2, situate high up in the vault, leading down in such a manner from the furnace chamber, *K*, to the heat-storage chamber, *R*, that the sides of the hearth are freely accessible. The chamber is built upon pillars, and hence the furnace is accessible also from below. The furnace is provided with doors, *F*, for introducing the metal to be melted, and with an upper and a lower tap-hole, S_1 and S_2. The lower hole, S_2, permits of the entire charge being

drawn off, whilst the upper tap-hole serves merely to draw off the upper portion of the melted steel, together with the slag. The zone, *Z*, in contact with the slag, is without

Fig. 132.



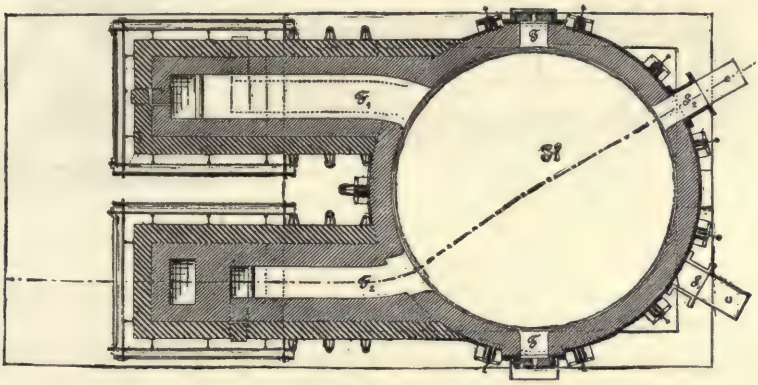


Fig. 133.

an iron coating, and is hence accessible on all sides and can be repaired even during work.

(4) Wrought or Bar Iron.

As already mentioned, wrought iron was formerly obtained by heating the ores with charcoal upon a hearth and forging out the spongy iron thus produced. This so-called "direct" process has been of late much improved, especially by Siemens, who used firstly a rotatory furnace and then a reverberatory (Figs. 134 to 137). The bottom of the melting chamber forms a tank, *s*, to collect the melted metal, and one side is a sloping hearth, *f*, upon which the mixture of ore, coal, and fluxes to be smelted moves downwards. For the convenient introduction of this mixture, a slit, *o*, is left free in the vault above the sloping hearth, and above it a space is set off, in which a large quantity of the mixture can be collected and sink gradually down through the slit as the charge already upon the hearth melts away. The tank, *s*, is fitted at different heights with three tap-holes *Z*, Z_1, and Z_2, the upper one being permanently open and serving for the continued removal of the slag, *Z*, is the general tap-hole for running off the melted iron from time to time, whilst the lowest hole, Z_2, is used only

if the furnace is to be completely emptied. Thus, a part of the iron-bath remains in the furnace, so that the slag never touches the bottom of the tank, and the iron, which is constantly being formed in the shape of fine globules, can sink down in the mass of metal upon the hearth. In order to render the slag suitably mobile and to remove impurities from the iron, lime, and potassium and sodium salts are added to the

Fig. 134. Fig. 135.

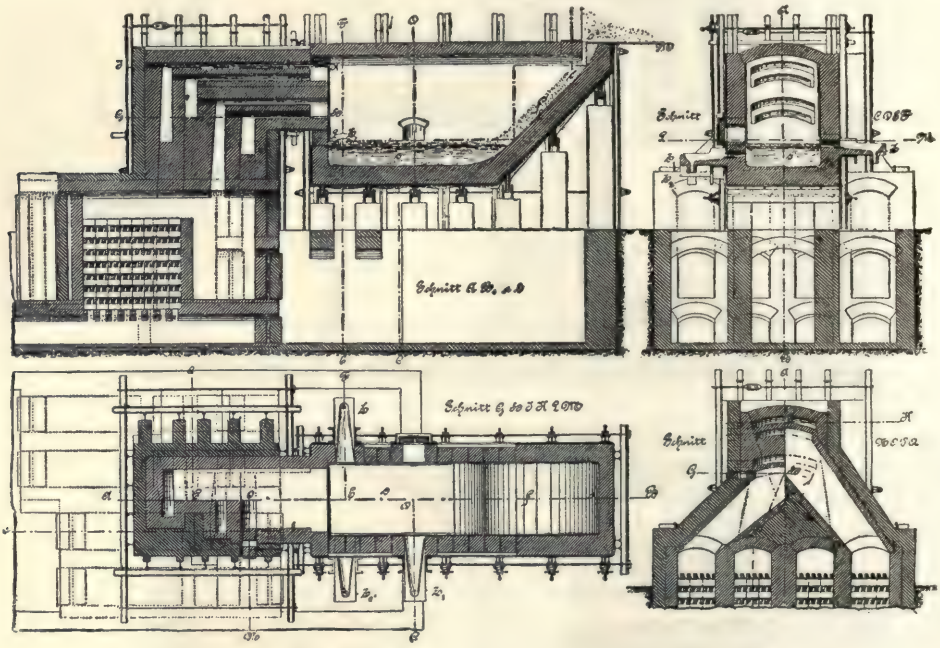


Fig. 136. Fig. 137.

Explanation of Terms.

FIG. 134.—*Schnitt* = Section A, B, *a*, *b*.
FIG. 135.—*Schnitt* = Section C, D, E, F.
FIG. 136.—*Schnitt* = Section G, H, I, K, L, M.
FIG. 137.—*Schnitt* = Section N, O, P, Q.

mixture, not generally, but under certain circumstances. The addition of such salts renders the slag more fit for the glass manufacture.

Opinions on the value of the direct processes are very varied. Ledebur considers them as unpromising. Westmann contests this view if the ores used contain at least 50 per cent of iron. For obtaining pig-iron, the following quantities of heat are needful:—

For reducing ores	1588
„ expelling H_2O and CO_2	158
„ reducing SiO_2 and P_2O_5	29
„ smelting iron and slags	774
To which come further for O ·0428 kilo. carbon taken up by the crude iron	173
Heat-units	2722

In the production of spongy iron the following items are dispensed with:—

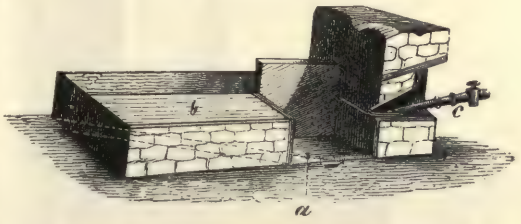
For expelling H_2O from fuel	82
„ carbon taken up by crude metal	173
„ reduction of SiO_2 and P_2O_5	29
„ half heat expended in smelting	372
Heat-units	656 = 24 %

By far the largest quantity of bar-iron is prepared from crude iron.

Refining Process.—This process depends on the removal by oxidation of the bulk of the carbon and the other foreign matters, especially silicon, from crude iron. Only white pig is used, as poor as possible in carbon, since before smelting it softens, remains for a long time as a thin liquid, and hence presents a larger surface to the oxidising agents. Its combined carbon burns more readily than the graphite of grey pig. This process may be effected either (1) on a hearth (sometimes called the German process), (2) in reverberatories (the puddling process), or (3) by forcing air into the melted crude iron (the Bessemer process).

In the hearth-refining process, white pig is melted in the four-sided, depressed fire-space, *a*, of the hearth, *b* (Fig. 138), in such a manner that it is not exposed to the blast until it is liquefied. The depression is lined with iron plates and receives the necessary current of air through the pipe, *c*. The fire-box is first filled with glowing charcoal, the blast is turned on, and the iron is laid upon the hearth and pushed down into the depression as it melts off at the end.

Fig. 138.



The air of the blast constantly burns the carbon of the crude iron to carbonic acid, and thus effects its decarbonisation. The sand adhering to the pigs, the silica formed by the oxidation of their silicon and that introduced by the ash of the charcoal, combine with the ferrous oxide simultaneously formed to bisilicate, $FeSiO_3$, the so-called "crude-slag" (68·8 per cent. ferrous oxide and 31·2 silica) which floats above the melted iron and is run off from time to time, though the iron is never left quite uncovered. This slag, mixed with anvil-dross (ferroso-ferric oxide), is used for the next operation to decarbonise the iron. In fining, all the other foreign matters contained in the iron, such as phosphorus, &c., pass into the slag in the state of phosphoric acid, &c. After the iron is melted the slag is drawn off, and the pieces of iron are exposed to the blast whilst being frequently turned. The slag now being formed becomes the richer in ferrous oxide as the metal becomes purer, and contains 73·7 per cent. ferrous oxide and 21·4 silicic acid. It is never crystalline, but compact, of a dark grey colour, and of a higher specific gravity than the crude slag. The whole mass of iron is made semi-fluid by an increase of the temperature to promote the separation of the slag. The fined lump (ball or bloom) is lifted out of the fire and brought under the lift-hammer. By its blows all particles of slag are forced out. The bloom is then cut into pieces, which are forged into bars. From 100 parts of pig iron there are obtained on the average 70 to 75 parts of bar iron.

The Swedish fining process acts at once upon small portions of iron only. The decarbonisation is effected by the oxygen of the air. Much fuel is consumed, and a not inconsiderable part of the iron is oxidised, but the iron obtained contains no slag, and is more compact.

The puddling process is, in fact, fining in a reverberatory furnace. In countries where charcoal cannot be used for fining crude iron on account of its high price, coal is used. As the immediate contact of coal with the iron must be avoided on account of the sulphur which it contains, reverberatory or puddling furnaces are used for effecting the elimination of the carbon. This is effected by agitation, either by hand or by machinery, or by means of a revolving hearth. Thus we have hand puddling, machine puddling, and rotatory puddling.

Preparatory to the puddling process is the refining, by which the free carbon is

brought into the combined state and the silicon is burnt. This refining consists in re-melting upon a bed of coke under the action of a blast. A grey pig-iron contained—

	Before Refining.	After Refining.
Carbon	2·5 ...	2·40
Silicon	1·0 ...	0·10
Sulphur	0·5 ...	0·40
Phosphorus . . .	0·7 ...	0·20
Manganese . . .	0·2 ...	0·05

Hence it appears that the proportion of carbon in crude iron is not reduced by refining, but the silicon is chiefly removed.

A puddling furnace is shown in front elevation in Fig. 139, and in Fig. 140 in section. The hearth, *A*, is a rectangular iron chest, into which air can stream in freely through the grate, *F*. Upon this hearth there is placed a layer of refining slag, to which forge scales have been added, and the mass is heated until its surface is softened. The pig-iron to be treated is heated until it is soft, spread about over the surface of the hearth by means of a stirrer, and heated with constant agitation (puddling). The working door, *D*, can be easily opened and closed. There appear small blue flames of carbon monoxide upon the pasty iron, and the metal becomes stiffer and tougher. The greater part of the slag formed during puddling flows away from the iron to the front of the furnace, down the inclined plane, *B*, and it is let off through an opening from time to time. When the puddling is completed the iron spread out on the hearth is collected into balls and freed from slag by the hammer.

Fig. 139.

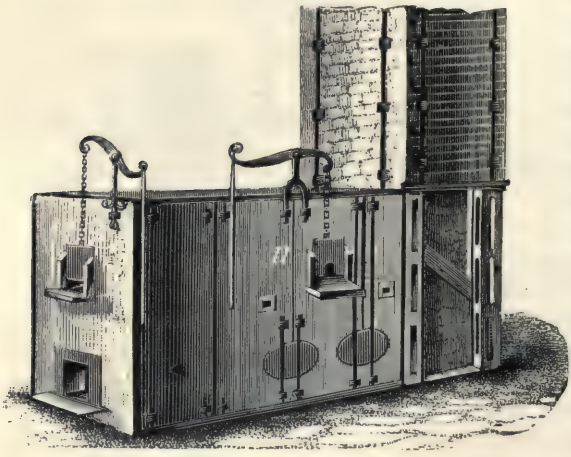
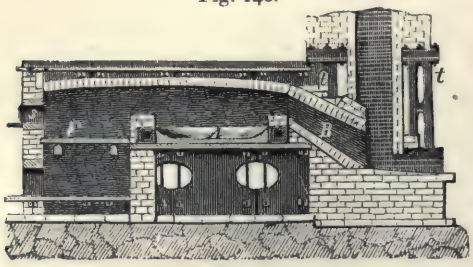


Fig. 140.



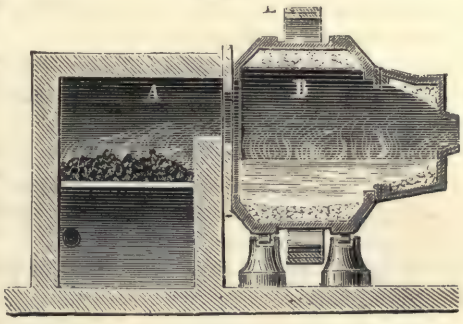
By the access of the air or of oxygenous fire-gases to the molten crude iron upon the hearth of the reverberatory, there is formed ferroso-ferric oxide, the oxygen of which removes the carbon of the crude iron in the form of carbon monoxide, which burns with a blue flame. As the mass is decarbonised it becomes less fusible, and there are formed in its interior solid masses of wrought iron, which increase in quantity and which are collected with the stirrer and slightly welded together. In practice the process is not so simple, because (1) it is not possible to bring all the ferroso-ferric oxide in contact with the carboniferous iron, so that oxide is easily left in the iron and prevents the coherence of its parts. To remove this superfluous oxide, crude slag is added, which is converted into refinery slag. The elimination of the oxide involves a loss of iron of 4 to 5 per cent., to which must be added 5 per cent. more by the combustion of the carbon; (2) another difficulty arises from the presence of blast-furnace slag, and of mechanically adhering silica, &c. During puddling the free silica unites with the blast-furnace slag; if this comes in contact with the ferroso-ferric oxide with deficient

carbon, it gives its silica partially to the ferroso-ferric oxide, forming with it a refinery slag, which adheres to the walls and the sole of the furnace, and a basic, very infusible blast-furnace slag, which remains mixed with the iron. The puddling process, as at present carried out, is quite unable to remove this slag. Recent studies of irons and slags in the various stages of the puddling process have proved that, in puddling, the oxidation of the combined carbon, silicon, sulphur, manganese, and iron, is effected much more by the combined oxygen of the slag and the fluxes than by the free oxygen of the air, which is especially active only at the period of melting. In the first portion of time after melting, the iron re-dissolves the non-combined carbon. Hence, the silicon is separated as silica, the proportion of combined carbon increases, and the graphite diminishes. At the same time, much of the manganese is oxidised. After this fining process is completed the boiling period sets in, with separation of carbon and partial reduction of iron, when the particles of iron separated are in the state of steel. In the third period, soft iron is formed with further decarbonisation, when the bulk of the phosphorus is separated out as iron phosphide and ferric phosphate, and passes into the slag.

Iron which contains too much phosphorus is purified by adding, during puddling, the so-called "Schafhautel's mixture" (manganese, common salt, and clay). According to Richter, litharge is better than manganese for oxidising the sulphur in crude iron. Superheated steam has also been proposed for the removal of sulphur. The volatilisation of sulphur and phosphorus has also been attempted by the addition of fluor-spar (Henderson's process), and of iodine compounds such as potassium iodide. Others add soda.

The tendency to displace manual labour more and more led, firstly, to the construction of the mechanical puddler, and, as the results were not completely satisfactory, to the invention of rotatory puddling furnaces, among which that of Danks (Fig. 141) deserves notice. The furnace, A, has a grate apparently similar to the common puddling furnace, but the necessary air is admitted also by a row of tuyères, placed above the grate. The rotatory hearth, B, consists of cast-iron segments, lined within with a mixture of iron-ore and bauxite. The rotatory hearth has a two-fold arrangement supporting two rails for the rollers upon which the apparatus rests movably, and a toothed wheel, E, to which the motion is communicated by means of a small engine. Whilst one opening of the hearth is in contact with the furnace bridge, the other serves for introducing the charge and taking out the finished blooms.

Fig. 141.



Bar-iron, Wrought or Malleable Iron, has a light grey colour and a granular and jagged fracture; its specific gravity is 7·60–7·90, that of chemically pure iron being 7·844. Its carbon is from 0·20 to 0·84 per cent., traces of which only are in a state of mechanical mixture.

Chemical examination of bar-iron give the following results—(1) English bars from South Wales, (2) soft bars from Magdesprung in the Harz, (3) Swedish Dannemora iron:

	1.	2.	3.
Iron	98·904	98·963	98·775
Carbon	0·411	0·400	0·843
Silicon	0·084	0·014	0·118
Copper	—	0·303	0·054
Phosphorus	0·041	—	—

Wrought iron, if heated to redness and plunged into cold water, does not become harder and more brittle, and can still be forged. It is much softer than grey or white pig, and can be easily filed, cut, planed, &c. It is far less fusible than crude iron; at a white heat it becomes so soft that two pieces can be united together by hammering, pressing, or rolling.

Iron shares this property of welding with platinum, palladium, potassium, and sodium. Iron is less easily welded the more carbon it contains. The bar-iron obtained by fining and puddling is more or less contaminated with foreign matter. If it contains sulphur, arsenic, and much copper, it is *red-short*, *i.e.*, it crumbles under the hammer at a red heat; silicon renders it hard and brittle, and the presence of phosphorus makes it cold-short, *i.e.*, it can be worked when hot, but when cold it breaks on bending. Calcium renders iron incapable of being welded. Hard, crystalline sorts are preferred for articles which have to resist friction and take a permanent polish. Tough, stringy irons serve for parts of machinery, for chains and anchors, &c.

The puddling process has lost much of its importance, and will probably be entirely superseded by the Siemens-Martin and the Bessemer processes, both of which produce steel as well as wrought iron. The treatment of 350 kilos. of iron in Danks' furnace appears feeble in comparison with the manipulation of 10,000 kilos. in the Bessemer converter.

STEEL.

Steel.—This substance differs from crude pig-iron and from bar-iron in the amount of carbon it contains: from crude iron, moreover, by being capable of welding; and, again, from bar-iron, by being comparatively readily fusible: in reference to the amount of carbon present, steel holds a position between crude pig-iron and bar-iron. Recent researches have revealed the fact that steel contains nitrogen; but whether this element really contributes to the peculiar properties of steel obtained from different sources is not a definitely settled point. Steel is obtained of various qualities by a number of processes, as will be seen in the following brief reference—

a. Directly from iron ores—

1. By the reduction of iron ores directly with the aid of fuel (chiefly charcoal), and a blast on the hearth, the steel being obtained in the form of lumps (so-called natural steel).
2. By the heating of certain iron ores along with coal, but without fusion (cementation steel from ores).
3. By the fusion of iron ores along with charcoal in crucibles (cast-steel from ores).

b. By the partial decarbonisation of pig-iron (rough steel, furnace steel, or German steel)—

4. By the refining (partial decarbonisation) of pig-iron by means of charcoal fuel on the hearth (sheer steel).
5. By treating pig-iron in reverberatory furnaces fed by coal or blast-furnace gases as fuel (puddled steel).
6. By forcing air through molten cast-iron (Bessemer steel).
7. By heating cast-iron to redness along with substances which will effect decarbonisation below the fusion-point of the metal; if the substances employed for partial decarbonisation are iron ores, the steel is called iron ore steel.
8. By melting crude cast-iron with such substances as those just mentioned.
9. By treating crude cast-iron with sodium nitrate (Heaton steel, Hargreave steel).

c. By imparting carbon to bar or malleable iron—

10. By ignition with carbonaceous matter, but without fusion (cementation steel).

11. By fusion with charcoal (cast steel).

d. By combination of methods *b* and *c*, as in fluxed steel—

12. By melting crude pig-iron and malleable iron together.

In India a kind of steel is still made directly from iron ores, and known as wootz (as to the composition of this substance, see the *Chemical News*, vol. xxii. p. 46); it is possessed of excellent qualities. The Japanese also understand the art of making steel of most excellent quality by rather rough and primitive means.

According to the degree of hardness we distinguish mild and hard steel, and according to its applications tool steel and machine steel.

The finery steel obtained by the partial decarbonisation of crude iron may be either—

(1) *Rough Steel* or *Natural Steel*, prepared chiefly from the "crude steel-irons"—a crude iron prepared from iron spar, and made in Styria, Carniola, Carinthia, &c., also as spiegeleisen, generally with charcoal, but partly with coke. Steel-fining is distinguished from iron-fining chiefly by the application of the blast, which is directed so that the carbon may be burnt gradually, and the workman has it in his power to interrupt the process at the moment when the steel is ready.

(2) *Puddled Steel.*—Steel may be produced by the puddling process from very different kinds of ore, and is furnished very cheaply for the wheels of locomotives, railway carriages, and other large and heavy objects.

(3) *Bessemer Steel.*—The pneumatic process invented by J. Bessemer, of Sheffield, in 1856, consists in forcing into liquid crude iron (whether direct from the blast furnace or such as has been re-melted in cupola or reverberatory furnaces) a strongly compressed blast of air. Without the addition of especial fuel a sufficient temperature is produced by the combustion of silicon, manganese, and iron to maintain the process and form ferro-silicate, which takes up ferroso-ferric oxide, and, as in the other refining processes, exerts an oxidising action upon the carbon and other foreign matter. Phosphorus is removed only by the *basic process* (Thomas & Gilchrist); sulphur to a small extent only; copper, nickel, and cobalt not at all. The process may be either continued until wrought iron is formed (which may then be converted into steel by the addition of spiegeleisen or ferro-manganese) or the carbon is removed only to the degree necessary to form steel.

On account of the energetic oxidation, the process is much more rapid than the fining on hearths and in reverberatories, and during the oxidation of the silicon a part of the carbon is burnt off also. To treat 10 tons of crude iron by this process requires from 10 to 20 minutes, whilst to puddle the same weight requires three days, and to convert it on the hearth about three weeks.

The best crude iron for the Bessemer process in converters with an acid lining (quartz, gannister) is a grey pig containing silicon and manganese, but as little phosphorus and manganese as possible. On forcing in strongly compressed air into this liquid iron, the silicon and manganese, along with some iron, burn first, and yield so high a temperature that it suffices to keep the mass liquid during the remainder of the process. The presence of manganese, which is oxidised almost simultaneously with silicon, retards the process. The behaviour of graphite in the first part of the process is similar, as it has to be converted into combined carbon before it is oxidised. In manganiferous grey pig the silicon seems to be chiefly combined with the manganese. In white pig, poor in silicon and containing carbon only in a state of chemical combination, the process is more rapid, which does not conduce to a good result. There is produced a thickly liquid steel mixed with slag, which cannot be rendered compact by forging. As a small percentage of sulphur is less hurtful in steel than in wrought-iron, good

coke-pig may give satisfactory results, especially if manganese is present, which helps to remove sulphur, but not phosphorus.

The apparatus consists of a pear-shaped converter of sheet-iron, A (Fig. 142). It is lined with a fire-proof mixture, and turns on two horizontal points by means of a toothed wheel, K, which catches into a toothed rod moved by the piston of a hydraulic press. At the bottom of the retort there is applied, by means of hydraulic pressure, a wind-chest, M, from which tuyères with forty-nine to eighty-four apertures convey the air, with thorough distribution, into the interior of the converter. The blast streams out from the pipe, L, through o, into a space round the pivot, d, passes downwards in the pipe, e, and enters the wind-chest, M, through the pipe, D, which is secured to e by means of a

Fig. 142.

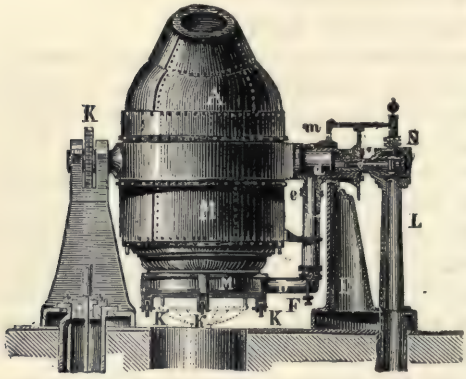
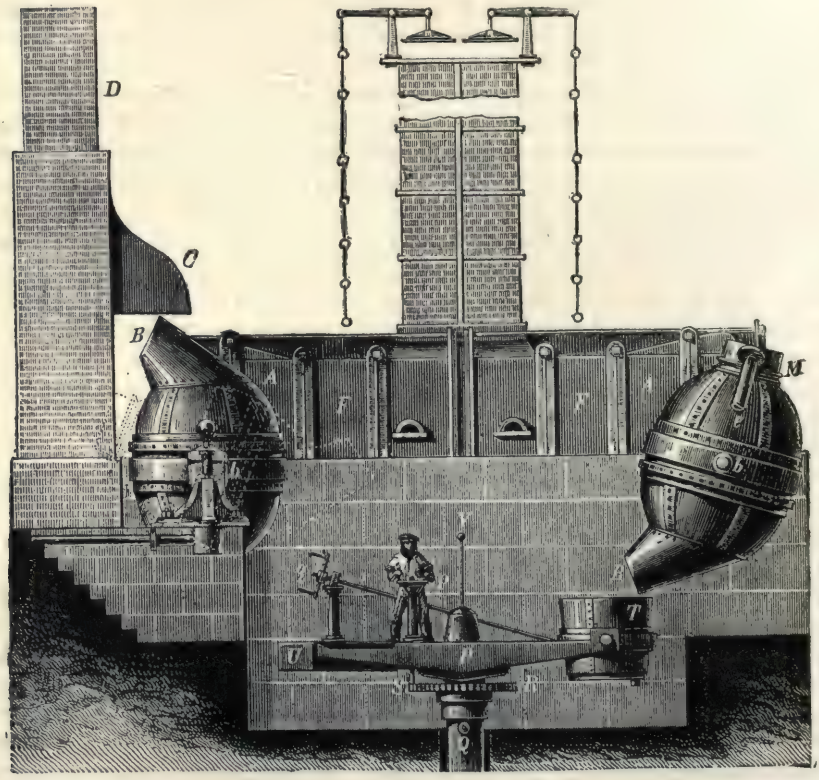


Fig. 143.



bent iron strap. The case, m, surrounding the pivot, d, rests upon the support, E, and is connected with the tube, o, by means of a stuffing box.

In working, the converter is first properly heated, and then from 3 to 10 tons of iron melted in reverberatories, or cupolas, *F* (Fig. 143), are run in a channel through the neck of the converter, *A*, inclined more than 90° (and shown in Fig. 143 by dotted

lines), in such a manner that it does not enter into and clog the tuyères at the bottom. The blast is turned on, and the converter is then raised to an upright position. The blast must have so strong a pressure that it forces the iron out of the jets of the tuyères, and distributes itself in fine streams. In the first period which thus begins (fining or slagging period), a temperature is produced exceeding the melting-point of wrought-iron; and silicon, manganese, and a part of the iron are oxidised; a slag is produced consisting of ferrous and manganous silicate; and the graphite is converted into combined carbon, but without the combustion of much of it. The indication for judging the process is chiefly the flame issuing from the mouth of the converter, *B*, into the chimney, *C D*, the sparks and the matter thrown out, as well as the spectroscopic character of the flame, and the appearance of samples taken. During the first four minutes no flame is visible, in the next two minutes there appears a small pointed flame, and, after six or eight minutes, an unsteady flame, with explosions. In these three intervals of time there are seen, by means of the spectroscope, at first a faint continuous spectrum from the sparks of ignited metal, then a light spectrum with flashes of the sodium line, and, lastly, a bright spectrum with a permanent sodium line, a red lithium line, and both the potassium lines.

With the explosions there begins the second period (the period of eruptions or boiling), in which the carbon is burnt by the abundant formation of ferroso-ferric oxide, in consequence of the more violent and copious formation of carbon monoxide; the mass rises up (boils), and slags and particles of iron are thrown forcibly out of the neck of the retort. The flame becomes bright and dense, then bright, but less dense below. With the spectroscope there are seen, in addition to the lines above mentioned, bright carbon monoxide lines in the red, the green, and the blue, and the bright lines in the green. In about fourteen minutes after the beginning of the process this period is at an end. In the third period the bath has become quieter; the eruptions have ceased, and much iron is burnt along with the carbon still remaining; this is indicated by a brisk rain of sparks, whilst the flame becomes less vivid and smaller. With the disappearance of the flame and the change of the green line of carbon monoxide into a continuous spectrum, the carbon is consumed within about eighteen to twenty minutes. The iron at the end of the third period is present as decarbonised iron (bar iron). If, as is generally the case, the production of steel is intended, the fourth period begins. For this purpose the blast is shut off, the converter is inclined, and so much liquid manganiferous spiegeleisen or ferro-mangan is introduced at the neck as will produce steel containing a given proportion of carbon. The converter is again placed upright, and the masses are allowed to mix, or the blast is turned on again for a moment to effect a more perfect intermixture. The converter is then turned to the right, and the steel is poured into the pan, *T*, and thence, by means of the hydraulic crane, *P*, into the moulds. By means of the wheels, *S* and *R*, the crane can be turned on the pivot, *Q*, and the pan, *T*, tilted by means of *q r*. The iron screen, *V*, is to protect the workman, and the counterpoise, *U*, keeps the plate, *P*, in equilibrium. The ferro-manganese is not merely to supply carbon to the iron, which has been decarbonised by the Bessemer process, but as the manganese present is more readily oxidised than the carbon, it is to keep the proportion of the latter constant.

Dahlems has followed the Bessemer process analytically in four Swedish establishments. (See Table.)

	Langshyttan.	Nykroppa.	Bangbro.	Westanfors.
Crude Iron.				
C	3·94	4·35	4·00	4·22
Si	1·14	0·88	1·02	1·06
Mn	0·64	1·15	1·83	5·12
Metal.				
I. time	2 min. 15 sec.	2 min. 30 sec.	3 min.	4 min. 15 sec.
C	4·02	4·01	4·03	4·02
Si	0·04	0·10	0·03	0·43
Mn	0·12	0·15	0·22	3·26
II. time	4 min. 30 sec.	5 min. 30 sec.	4 min. 45 sec.	8 min. 35 sec.
C	1·10	1·00	0·90	1·30
Si	0·03	0·05	0·03	0·12
Mn	0·12	1·15	0·12	0·85
III. time	5 min. 30 sec.	6 min. 30 sec.	5 min. 45 sec.	9 min. 20 sec.
C	0·05	0·08	0·10	0·55
Si	0·01	0·04	0·03	0·07
Mn	0·06	0·08	0·09	0·43
Slag.				
I.				
Ferric oxide	34·72	13·50	14·20	4·20
Mangan oxide	13·95	29·76	26·31	46·38
Magnesia	0·24	0·23	0·22	0·54
Lime	2·60	0·42	0·62	1·26
Alumina	0·78	2·28	2·86	3·08
Silica	48·76	53·26	55·26	45·87
II.				
Fe_2O_3	21·08	9·34	18·52	6·24
Mn_2O_3	13·48	23·70	31·01	52·26
Magnesia	0·30	0·28	0·14	0·29
Lime	3·25	0·60	0·38	0·70
Alumina	0·98	3·90	2·70	2·49
Silica	59·92	62·34	47·20	39·07
III.				
Fe_2O_3	35·82	30·60	31·19	9·45
Mn_2O_3	12·29	21·39	25·43	48·92
Magnesia	0·21	0·21	0·11	0·46
Lime	2·35	0·38	0·32	1·00
Alumina	0·72	2·14	2·24	2·94
Silica	48·48	44·54	40·50	37·63

In the basic process (of Thomas & Gilchrist), the converter is lined with a mixture of burnt dolomite and tar. Besides freshly burnt lime is introduced into the heated converter to about 10 per cent. of the intended charge of metal; the liquid iron is then run in and the blast is turned on.

Finkener showed that first the proportion of silicon and manganese decreases, then that of carbon, and lastly, that of phosphorus and manganese, if the latter has not already disappeared along with the silicon. The removal of these substances is the consequence of their oxidation, and of the property of the products of oxidation to separate from the liquid iron which, however, can take place only when the substances eliminated under the above circumstances have no especial decomposing action upon each other. Experiments show that the carbon escapes chiefly as carbon monoxide, with a small proportion of dioxide, which is such that the transit of carbon dioxide to the iron is compensated by the carbon given to the iron by the carbon monoxide. The proportion between carbon monoxide and carbonic acid may vary with the temperature and the quality of the iron exposed to the action of the gaseous mixture, but the carbonic acid does not entirely disappear except the proportion of carbon in the iron is

very high. The phosphorus is oxidised to phosphoric acid along with iron enough to form a ferrous phosphate, containing 3 mols. iron to 1 mol. of phosphoric acid. A compound of phosphoric acid with a smaller proportion of iron cannot separate from the liquid iron, as it would be decomposed. The silicon is converted into silicic acid, which, like the phosphoric acid, enters into the slag as a ferrous compound, containing 1 mol. silica to 1 at. iron or manganese. The oxygen entering into the liquid mass will at first burn all the constituents with which it comes in contact, but of the compounds formed only those will remain undecomposed which are equally fusible with the liquid mass. As long as silicon is present the carbon will not decrease; the carbon monoxide as it is formed decomposes, forming silicate and metallic carbide. The iron silicide has such a reducing action that it reduces a part of the iron present in the normal ferrous silicate to the metallic state. The phosphate, which is more readily reduced, cannot remain; it is decomposed in contact with the metallic silicide to silicate and metallic phosphide. A decrease of the phosphoric acid does not occur so long as silicon is present. Iron is protected from oxidation by manganese, just as is phosphorus by silicon; the chief product of the oxidation is, in the beginning, manganous bisilicate. After removal of the silicon, carbon monoxide appears, with a proportion of carbon dioxide, which increases somewhat as the carbon dioxide decreases. Manganous and ferrous phosphates are found in perceptible but not large quantities, and are chiefly decomposed by the iron carbide which still exists. This reduction can only be ascribed to the mixture of carbon monoxide and dioxide, on the supposition that the reducing power of the mixture increases more rapidly as the temperature rises than that of iron carbide. Against the assumption that carbon monoxide has a reducing action upon ferrous phosphate, must be put the small proportion of phosphorus in the metallic iron selected from different slags. If iron carbide is the reducing agent, the iron phosphide formed immediately comes in contact with iron, and there is no inducement for the formation of an iron rich in phosphorus. When the carbon has disappeared the separation of the iron phosphate is effected. The iron sulphide remains undecomposed even after the removal of the phosphorus. After the addition of spiegeleisen the proportion of phosphorus increases by the reduction of ferrous phosphate by iron carbide. Fig. 144 shows the changes taking place in iron, and Fig. 145 those in slag, according to an experiment made at Hörde.

According to Hilgenstock, the quadri-basic calcium phosphate, $Ca_4P_2O_9$, is the supporter of the basic process. In a crude iron which, when put into the converter, contained 3 per cent. phosphorus, 1 per cent. manganese, 0·15 per cent. silicon, 2·7 carbon, and 0·15 sulphur, the silicon is soon removed, the combustion of the carbon begins, and with it the oxidation of the manganese and the phosphorus, so that after decarbonising it retains 0·01 to 0·02 Si, 0·10 to 0·15 C, 0·2 to 0·3 Mn, 1·5 to 2 P, and 0·10 to 0·12 S. After the dephosphorising process, during which the metal mostly requires to be cooled, the bath retains—Si, 0·08 to 0·01; C, 0·06 to 0·14; Mn, 0·07 to 0·25; P, 0·05 to 0·07; S, 0·08 to 0·09, but as much as 0·3 per cent. of oxygen.

After the bath has been reduced by ferro-manganese, the finished steel contained Si, 0·08 to 0·01; C, 0·10 to 0·20; Mn, 0·35 to 0·45; P, 0·05 to 0·09, and S, 0·04 to 0·06.

Among the oxidation products silicon as manganous silicate is not reduced at the initial low temperature of the bath, or afterwards at a higher temperature as calcium silicate by any constituents of the bath; hence the rapid and almost total disappearance of the silicon; silicon if once oxidised remains in the slag as a basic silicate. Carbon monoxide disappears without any noteworthy reductive action either upon metal or slag, so that, save the action of the current of the air, we have only the reactions of the two (igneous) liquids, the metal and the slag, to consider. At the beginning of the dephosphorising process we have to do with them only. After the bath is decarbonised the manganese is reduced to a few tenths and the phosphorus to

one-half. The oxidation and separation of the phosphorus takes place as tribasic ferrous phosphate. The iron phosphate is at once converted into calcium phosphate by the more powerful base lime, and there is formed the quadri-basic phosphate, which is not reduced by metallic iron. The liberated ferrous oxide is again reduced by contact with phosphorus in the bath, so long as the proportions are suitable. If there is from 0·5 to 0·3 per cent. of phosphorus in the bath no notable quantity of

Fig. 144.

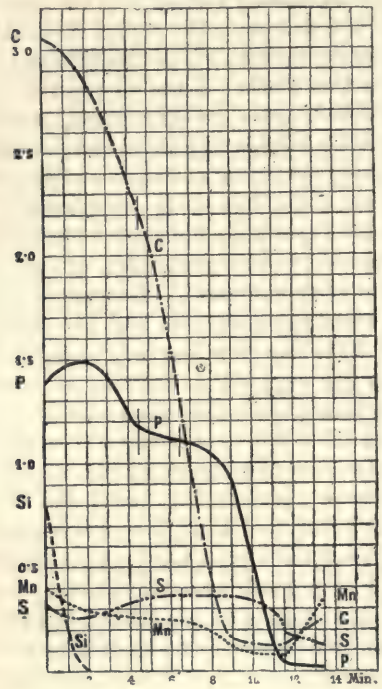
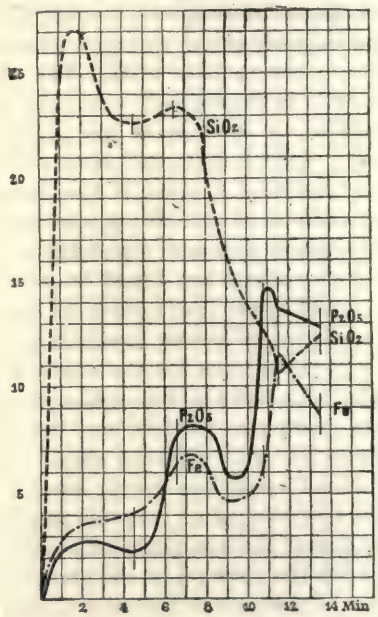


Fig. 145.



ferrous oxide remains unreduced, and not until afterwards does the iron increase in the slag. It is one of the grandest industrial reactions that in masses of crude iron of the weight of ten tons the phosphorus in contact with three tons of slag is reduced within a few minutes to some tenths per cent.

The Slag.—The basic process yielded in 1886, in round numbers, 400,000 tons of slag containing from 30 to 35 per cent. calcium phosphate; its utility in agriculture is therefore of the highest importance. At first the slag was prepared in a variety of ways; now it is simply ground to a fine powder, since experience has proved that it is soluble in the soil.

In experiments on the value of the phosphoric acid in the "Thomas slags," Märcker proved that when finely ground it had 56 per cent. of the efficacy of the soluble phosphoric acid in superphosphates, even on superior soils. On moorland soils it was of equal value to the "precipitated phosphates." Slag has no injurious effects upon the crops. The only condition is very fine grinding.

The Siemens-Martin Process.—In this process the decarbonising agent is iron oxide, iron ores, and iron waste. The crude iron is melted in a Siemens reverberatory, and it is introduced into the bath, covered with a layer of slag, old iron, &c., until a sample drawn shows that the entire mass has assumed the fibrous nature of bar-iron. By adding a certain quantity of crude iron the entire mass is converted into steel. The table on p. 140 shows the working of this Siemens-Martin process at the rolling works at Graz.

Very important experience has been gained with the use of water-gas in this process. The furnaces employed at Witkowitz have good heat-stoves (Figs. 146 to 149);

Fig. 146.

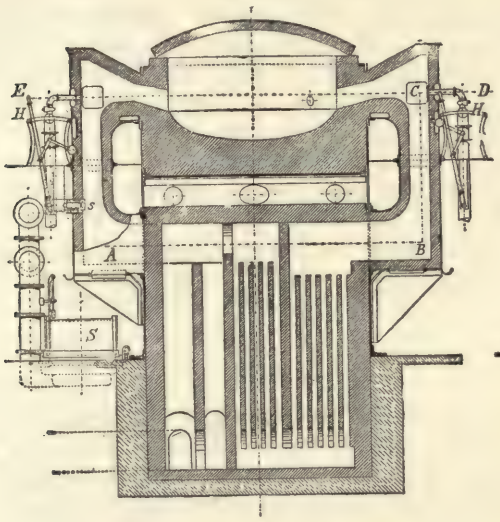
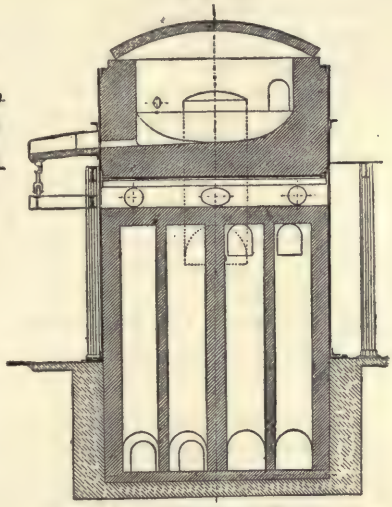


Fig. 147.



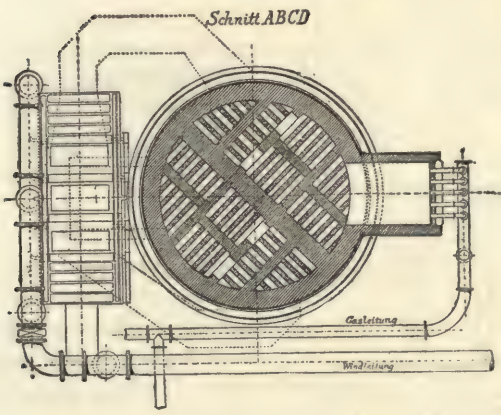


Fig. 148.

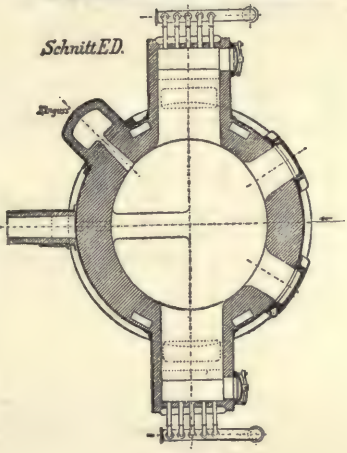


Fig. 149.

Explanation of Terms.

Schnitt ABCD	Section ABCD.	*Schnitt ED*	Section ED.
Gasleitung	Gas-piping.	*Einguss*	Inflow.
Windleitung	Air-pipe.		

they are round and enclosed with a sheet-metal screen; the bottom is cooled with air. The vaults of the Martin furnaces can be lifted off. For this purpose a powerful crane is fixed between the two Martin furnaces, and it serves also to raise the steel pan to the necessary level. Each gas tuyère has a cock connected by a rod to the rest in such a manner that all the cocks can be turned at once. The two gas-pipes from which the gas tuyères branch off to each furnace have throttle valves. The air is forced by a blast under a small bell, which always maintains the necessary pressure (110 mm., equal to the pressure of the gas). The air-pipes branch off in two arms at each furnace and discharge into the furnace channels through which the flue-gases pass from the regenerators to the chimney. Each of these channels can be shut alternately by the slide, *S*, whilst the other is connected with the flue.

Charge.	Iron.				Slag.			
	C.	Mn.	Si.	SiO_2.	Al_2O_3.	MnO.	FeO.	CaO.
6.40 A.M., 1st charge of— 2100 kilos. white pig, 1500 „ grey pig, 1000 „ steel ends,								
Sample when smelted	1·13	0·14	0·01	42·56	1·46	28·39	29·47	
9.10 A.M., 2nd charge— 500 kilos. hoop-iron, 500 „ turnings, 2000 „ old boiler plates, 1000 „ old rails,								
Sample when smelted	0·69	0·11	—	42·94	1·53	22·23	31·47	
11.20 A.M., 3rd charge— 3900 kilos. old rails,								
Sample	0·27	0·13	—	48·03	1·76	18·48	30·15	0·78
12.20 P.M., sample	0·20	0·12	—	47·87	2·34	19·53	29·99	
1.40 P.M., sample	0·12	0·08	—	48·90	2·01	19·37	28·88	
1.45 P.M., added 120 kilos. silico ferro-manganese,								
Average sample of day's work . .	0·31	0·45	0.01	49·63	—	20·89	25·42	

In a water-gas Martin furnace 200 hectokilos of steel were produced in twenty-four hours. The consumption of gas is about 8 cubic metres per minute. The air in the regenerators is heated to 1200° to 1400°, whilst the temperature in the furnace is near the melting-point of platinum. The heat of the escaping gases behind the regenerators is still 400° to 500°; 60 cubic metres of water-gas are used for 100 kilos. of finished steel, including the preliminary heating, &c., of the bottom.

Fig. 150.

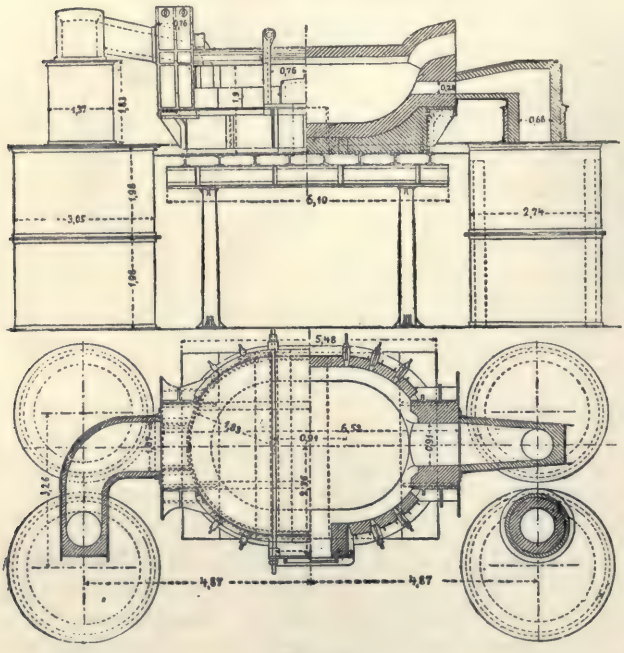
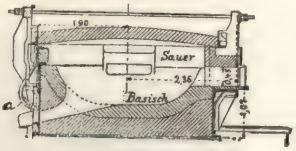


Fig. 151.

Fig. 152.



Sauer Acid.
Basisch Basic.

In a common Siemens-Martin stove 50 kilos. of Ostrau coal are used for 100 kilos. Hence, for the same amount of work, the water-gas Martin furnace consumes only 47 per cent. of the quantity of heat which an ordinary Siemens-Martin furnace requires.

Basic Hearth-Smelting.—This process promises to be of great importance now the difficulties of producing a lining of magnesia have been overcome. Figs. 150 to 152 show a furnace suitable for charges of 12 tons. The vault, built of an acid stone, is supported by a strong furnace frame, whilst the upper acid part of the hearth-walls consists of separate parts built in boxes, which, if needful, *e.g.*, for mending the furnace, can be turned back on the arm, *a*, which rotates on the furnace-frame, or may be

entirely changed. By this arrangement all strain is removed from the basic hearth-walls—a point of great importance, as basic materials are mostly very sensitive to pressure. The basic stones consist of burnt dolomite, and are submitted to a pressure of 150 tons on the flat side, and then immediately built into the furnace and heated as quickly as possible. In small furnaces the basic walls reach up to the vault, otherwise only up to the upper angle of the charging apertures; below the slag-line 8 to 10 per cent. of sand is mixed with the basic mass. The upper, changeable part of the walls (45 centimetres high) is built of 2000 ordinary acid stones, separated from the basic lining by a layer of chrome iron and retort-coke, mixed with lime and tar. The vault, consisting of 3000 acid stones, is luted with clay to the walls.

When the furnace has been duly heated it is charged with ore or anvil-dross and lime, upon which crude and wrought iron are laid. During heating care must be taken that the slags are sufficiently basic. The duration of the heat is generally shorter than that of an acid furnace, since the dephosphoration is complete as soon as the iron is entirely melted. It might then be tapped, only that a higher temperature is necessary for compact castings, and a further decarbonisation is often necessary. Hence it is proposed to heat with water-gas, in the expectation of finishing a process in four and a half hours.

Dolomite powder, raw or burnt, and mixed with 8 to 12 per cent. of sand, is used for repairs.

Further experiments were made on a 5-ton Martin furnace with a basic lining. Two charges were melted of 60 parts crude iron, 30 parts granulated steel, and three parts spiegeleisen, and a third of 70 crude iron, 30 steel, and 4 spiegeleisen. After the mass was in flux a sample of metal and one of slag was drawn every half-hour, and besides a sample of slag, A, after the charge was one-third melted, and another, B, after it was two-thirds melted.

Metal.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	12.	13.	Steel.
C	1·760	1·680	1·390	1·260	0·840	0·510	0·400	0·220	0·090	0·075	0·075	0·070	0·140
Si	0·075	0·075	0·070	0·090	0·080	0·060	0·060	0·040	0·035	0·030	0·018	0·010	trace
P	1·400	1·370	1·320	1·110	0·990	0·900	0·810	0·700	0·620	0·460	0·180	0·085	0·075
Mn	0·100	0·100	0·115	0·090	0·100	0·080	0·090	0·075	0·085	0·100	0·125	0·120	0·370
S	0·180	0·169	0·162	0·150	0·145	0·140	0·145	0·147	0·137	0·133	0·120	0·111	0·089

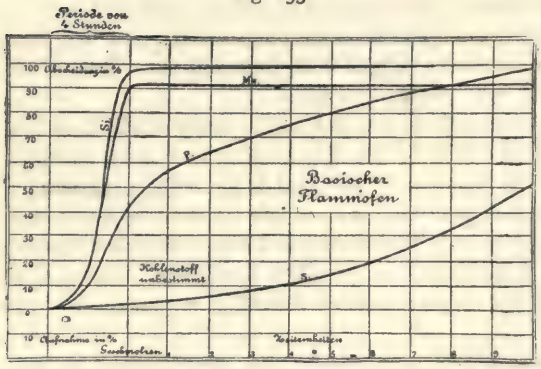
Slag.	A.	B.	1.	2.	3.	4.	5.	6.	7.	8.	13.
SiO_2 . . .	14·40	—	23·60	—	—	—	—	—	—	—	17·40
Fe_2O_3 . . .	6·81	0·40	0·73	3·80	0·77	0·90	2·60	2·30	1·60	1·17	1·64
FeO . . .	44·20	21·50	8·07	6·75	7·28	6·21	6·35	7·38	4·77	5·31	4·53
Al_2O_3 . . .	6·80	—	7·00	—	—	—	—	—	—	—	7·50
MnO . . .	2·04	—	8·15	—	—	—	—	—	—	—	4·60
CaO . . .	14·00	—	38·10	—	—	—	—	—	—	—	44·00
MgO . . .	0·84	—	1·28	—	—	—	—	—	—	—	2·80
P_2O_5 . . .	10·00	—	12·45	—	—	—	—	—	—	—	15·75
Fe . . .	38·90	17·09	6·79	7·93	6·10	5·40	6·90	7·41	4·80	4·90	4·63

The separation of the substances in question from the iron in the basic reverberatory, the basic converter, and the puddling furnace is shown in the diagrams Figs. 153 to 155. The processes in the basic reverberatory have, as the lines show, the greatest resemblance to those in the puddling furnace. The lines of phosphorus and sulphur run in a similar manner, a difference existing only in the quantities of these substances eliminated. In the Siemens process 18 to 19 per cent. of phosphorus is separated more than in the puddling furnace; but the puddling furnace oxidises 5 per cent. more sulphur than the basic reverberatory. In both furnaces almost the total silicon and manganese are conveyed into the slag in the first two periods of time, and about 40 per cent. of phosphorus is removed. The lines indicating the oxidation in

the basic converter take a quite different course from those in the basic reverberatory, although the results obtained by the oxidation are equal. The silicon line only resembles that of the other processes. The separation of carbon in the basic reverberatory is so irregular that it cannot be represented by a line.

Carbonisation Steel.—The second principal kind of steel (cement steel) is produced by the prolonged ignition of bar-iron along with carbonaceous substances, which generally contain at the same time, nitrogen. To obtain normal cement steel it is necessary to use good bar-iron. The Swedish iron (from magnetic ore and red hæmatite) is brought in large quantities to England for conversion into cement steel, as even the best English iron is suitable only for ordinary steels.

Fig. 153.



Explanation of Terms.

Periode von 4 Stunden	Period of 4 hours.
Abscheidung in %	Separation in per cents.
Kohlenstoff unbestimmt	Carbon not determined.
Aufnahme in % Geschmolzen	Taken up in per cent. fused.
Zeiteinheiten	Units of time.
Basischer Flammofen	Basic reverberatory.

The process for the manufacture of cement steel is as follows:—The iron bars are laid in layers, along with the carbonaceous powder, in earthen boxes, closed air-tight. Two such boxes (a pair of pots) are placed in a furnace which is fired with coal, rarely with wood, and kept at a red heat for one to three weeks. It is then let cool, and the bars are taken out. A furnace contains about 15 tons of iron. About 5 per cent. of carbon penetrates by molecular migration without the iron being fused; the action of gases falls quite into the background

Sheer Steel.—Both crude and cement steel are very unequal in their composition, and cannot therefore be used immediately, but must be rendered uniform by refining.

Fig. 154.

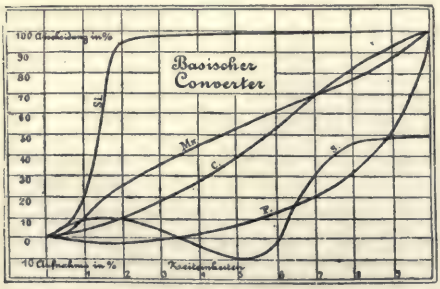
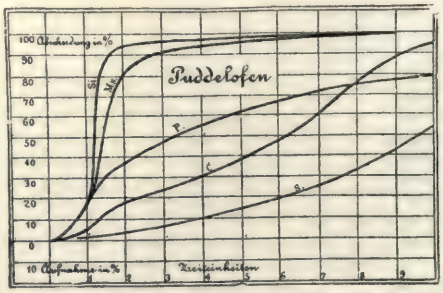


Fig. 155.



Explanation of Terms.

Basischer Converter	Basic converter.	*Puddelofen*	Puddling furnace.
Abscheidung in %	Matter eliminated in per cents.	*Abscheidung in %*	Matter eliminated in per cents.
Aufnahme in %	Matter taken up in per cents.	*Aufnahme in %*	Matter taken up in per cents.
Zeiteinheiten	Units of time.	*Zeiteinheiten*	Units of time.

To this end the crude bars are forged out to thin, flat slips, which are thrown into cold water when red hot; several of them are collected in a sheaf, heated to whiteness, and again wrought out under the hammer or between rollers. For cement steel a simple re-melting is more suitable.

Cast Steel.—This material, so widely used in modern industry for the manufacture

of cannons, tyres for railway wheels, axles, anchors, pump-rods, and for tools, is produced by re-melting finery steel, Martin steel, Bessemer metal, or carbonised steel. Every desired property can be obtained by a due selection of materials.

The melting is effected in fire-proof crucibles (without a blast) in a fire of coke, or in a coal reverberatory, or with a gas fire and Siemens regenerators. The melted steel is cast in bars in iron moulds. When cold, the bars are again heated to redness, wrought out under the hammer or between rollers. The metal thus treated is refined cast steel.

Run Steel.—This kind is formed by melting together crude iron and wrought-iron. The quality of steel thus obtained (known in Italy as Glisenti steel) depends on the quantity (and quality) of the wrought-iron used.

As a welding agent for cast steel, a mixture of borax with sal-ammoniac and potassium ferrocyanide is in use.

A remarkable phenomenon is the infiltration of cast blocks. A steel block had above and below the following compositions—

	Top.		Bottom.
Fe	98·304	...	99·638
C	0·760	...	0·350
Si	traces	...	traces
S	0·187	...	0·044
P	0·191	...	0·044
Mn	0·558	...	0·514
	100·000		99·990

Iron and steel castings not unfrequently contain hollows, the outer layer especially containing numbers of bubbles, *a* (Fig. 156). The bubbles more in the interior arise during progressive cooling, having a pear shape, with the point turned outwards, and forming the series *b*. Other hollows, *c*, appear in the midst of the casting, and decrease from above downwards; *a* and *b* arise from the liberation of gas dissolved in the liquid metal, but *c* in consequence of the condensation of the iron on becoming solid. Manganese, silicon, and magnesium have been used as a remedy for these bubbles.*

Fig. 156.



Steeling.—For certain technical purposes it is sufficient to convert iron into steel superficially. This steeling or case hardening is effected by cleaning the surface of the article with emery, and heating it, along with a carbonaceous powder, in an air furnace without a blast. Or the surface iron may be steeled by covering it when red hot with potassium ferrocyanide or with a mixture of clay and borax.

Properties of Steel.—Steel is generally of a pale greyish-white colour, moderate lustre, granular, and of homogeneous fracture; the better the sample the finer is the grain. The granular texture of steel is characteristic; good mild steel has never the coarse grain of grey crude iron nor the fibrous texture of wrought-iron. Hardened steel resembles in its fracture the finest silver, and the grains can scarcely be distinguished with the naked eye. Like wrought-iron, it may be cut and welded when hot, but it must be cautiously heated to avoid decarbonising. It is fusible like cast-iron. Its specific gravity is 7·62 to 7·92, and is diminished on tempering—*e.g.*, from 7·92 to 7·55. Its proportion of carbon varies from 0·25 to 2 per cent. With higher proportions of carbon, its solidity and hardness increase, but its elasticity decreases. It contains no graphite. If quenched when ignited, it becomes

* A small addition of aluminium has latterly been found successful.

harder and brittle, so as to scratch glass and resist the file. Polished steel assumes various colours when gradually heated. These colours are used for determining the temperature and the consequent degrees of hardness. For this purpose metallic baths are used, heated to their melting-point. Into such melted metal the steel is plunged until it assumes the temperature of the bath. The following table gives the composition of the baths found convenient for different kinds of cutting and piercing instruments :—

Instruments.	Metal Bath.		Heat.	Colour.
	Lead.	Tin.		
Lancets	7·0	4	220°	pale yellow
Razors	8·0	4	228	straw colour
Penknives	8·5	4	232	brown yellow
Scissors and chisels	14·0	4	254	brown, purple spots
Axes, pocket-knives, plane-irons	19·0	4	265	purple
Blades, watch-springs, crinoline steel	48·0	4	288	light blue
Daggers, gimlets, rapiers, fine saws	50·0	2	292	royal blue
Hand-saws	boiling linseed oil		316	black blue

The lower the heat of the steel, the harder, but the more brittle, it remains. It cannot be denied that iron may be converted into steel by other substances besides carbon, which may probably be replaced by its near ally, boron, and possibly by silicon.

Admixtures of other materials confer upon steel valuable properties; thus tungsten steel owes its peculiar firmness to the presence of tungsten. Samples of tungsten steel (I.) and tungsten iron (II.) had the following composition—

	I.		II.
Fe	85·000	...	68·363
W	11·028	...	28·181
Mn	1·493	...	0·986
Co and Ni	trace	...	trace
Si	0·263	...	0·233
P	0·007	...	0·008
S	trace	...	trace
C	2·147	...	1·882
	99·938	...	99·653

Similar assertions are made concerning titanium- and chromium-steels, but whether with justice must remain for the present undecided.

A celebrated kind of steel is that of Damascus, used for the Damascus sword-blades, though the raw material was brought from Cabul. If its surface is moistened with an acid it displays an uneven veining, a property which is not lost by re-melting. Such steel, Wootz, is made in India by the natives. Crude iron, obtained by a very imperfect process, is broken up, mixed with 10 per cent. of the chipped wood of *Cassia auriculata*, placed in a crucible, covered with leaves of *Asclepia gigantea;* the crucible is coated with moist clay and heated in a furnace for two and a half hours, at the lowest available temperature. The steel thus obtained is re-heated before forging.

Two samples of Wootz had the following composition—

Combined carbon	1·333	...	0·0167
Graphite	0·312	...	0·0035
Si	0·045	...	0·0006
S	0·181	...	trace
Al	—	...	—
P	—	...	trace
As	0·037	...	—

Steel Engraving.—For engraving and etching on steel there are used plates of

cast steel, which are decarbonised on the surface, and after engraving are re-converted into steel.

An excellent fluid for etching is a solution of 2 parts iodine and 5 parts potassium iodide in 40 parts of water.

MANGANESE.

Occurrence.—The most important ore of manganese is pyrolusite, MnO_2, often spoken of in commerce simply as "manganese." It contains generally small quantities of baryta; silica and water, and sometimes larger proportions of nickel, cobalt, and some thallium. Other manganese ores are braunite, Mn_2O_3, manganite, $Mn_2O_3H_2O$, hausmannite, in which the manganous oxide is in part replaced by potassa, baryta, magnesia, and cuprous oxide, and manganese-spar, $MnCO_3$. The manganese of commerce is often a mixture of pyrolusite, hausmannite, braunite, &c.

Preparation.—Manganese is prepared by reducing the ores in crucibles. Latterly it has been obtained on the large scale along with a larger or smaller proportion of iron as ferromanganese. Its preparation is effected in blast furnaces with a plentiful addition of lime. Manganese has a great tendency to pass into the slags, so that in a well-worked blast furnace from 40 to 50 per cent. of the manganese in the ores is to be found in the slags, which contain from 6 to 9 per cent. of metallic manganese. To extract more than 60 per cent. of the ores is rarely remunerative, as the consumption of coke is very high and the spiegel acquires grey spots by taking up silicon.

	Ferromanganese.			Crude Manganese.
	I.	II.	III.	
C	6·21	6·600	5·874	6·0–6·5
Si	0·28	0·093	0·210	0·5–1·2
P	0·06	0·300	0·305	
Cu	0·14	—	0·090	
Mn	69·64	81·240	57·608	90·0–92·0
Fe	23·25	12·000	35·031	0·5–1·5
Co	—	—	0·070	

Alloys of copper and manganese have been produced by Gersdorff and then by Schröter, by heating a mixture of copper, manganic oxide, and carbon in a crucible. They are very hard and take a polish; their colour is white to rose. Manhés has used them to reduce cuprous oxide in fining copper. Manganese-silver, an alloy of 80 parts copper, 15 manganese, and 5 zinc, is white, works well and takes a fine polish.

COBALT.

Cobalt is chiefly met with as speiss, $CoAs_2$, and as cobalt glance, CoAsS. Recently metallic cobalt has been prepared on a large scale at Iserlohn, and at Pfannenstiel, near Aue (Saxony). It has a silvery white colour with a reddish cast, a higher lustre than nickel, and polishes well. When obtained by electrolysis or by reduction as a pure metal, it is flexible and ductile, but as found melted under ordinary circumstances it is porous and crystalline, and can neither be hammered nor rolled. This evil is due, according to Fleitmann, to the absorption of carbon-monoxide, and can be removed by the addition of 0·1 per cent. of magnesium. It fuses at a very high temperature. At a white heat steel and iron may be welded together with cobalt, and iron, plated on both sides with cobalt, can be rolled out very thin. It is slowly dissolved by dilute acids; more rapidly by nitric acid and *aqua regia*.

Cobalt Colours.—The ores to be worked for cobalt colours are roasted, and are then called safflor or zaffre. According to their purity, they are distinguished as ordinary (SO), medium (MS), and fine (FS and FSS). They consist essentially of cobalt oxide,

nickel, arsenic, with traces of manganese, and bismuth oxides, &c. In Sweden, zaffre is prepared by precipitating a solution of cobaltous sulphate with a solution of potassium carbonate. From zaffre are prepared: smalts, cobalt ultramarine, cœruleum, Rinmann's green (cobalt green, or Saxon green), with which are connected cobalt yellow, cobalt violet, and cobalt bronze.

Smalts.—Glass is coloured blue by compounds of cobalt. If zaffre (impure cobalt oxide) is fused with silica and potash, we obtain a deep-blue glass, which, when finely ground, is known as smalts. The best sort, *i.e.*, that richest in cobalt, is called king's blue. According to Ludwig it contains:—

	Norwegian. Couleur.		German. Eschel.		Coarse.
Si	70·86	...	66·20	...	72·11
Co	6·49	...	6·75	...	1·95
K and Na . . .	21·41	...	16·31	...	1·80
Al_2O_3	0·43	...	8·64	...	20·04

It contains, besides, small quantities of ferrous and nickelous oxide, lime, arsenic acid, carbonic acid, and water, sometimes also lead. Soda cannot be used in place of potash in the manufacture of smalts, as soda cobalt glasses have not a pure colour.

Smalts are used for blueing paper, linen, and starch, and for colouring and painting on glass and porcelain, and for enamels.

Cobalt Speiss.—As in roasting cobalt ores the heat is not prolonged sufficiently to oxidise the nickel present in the ores, it melts with the other metals and the arsenic to a white mass, with a reddish cast, a strong metallic lustre, and a finely granular fracture. It consists of 40 to 56 parts of nickel, 26 to 44 of arsenic, along with copper, iron, bismuth, and sulphur.

Cobalt Ultramarine.—This substance, also known as Thénard's blue, is a pigment consisting of alumina and protoxide of cobalt. Curiously enough, this pigment has been discovered and prepared at three several periods and localities by different people; first by Wenzel, at Freiberg, Saxony; next by Gahn, at Fahlun, Sweden; and lastly, simultaneously at Paris and Vienna, by Thénard and von Leithener. The pigment is prepared either by mixing solutions of alum and a salt of protoxide of cobalt, precipitating the mixture by a solution of carbonate of soda; or by the decomposition of aluminate of soda by means of chloride of cobalt. The ensuing precipitate, consisting of an intimate mixture of hydrate of alumina and hydrate of protoxide of cobalt, is first well washed, then dried, and heated for some time. The pigment thus produced is, when seen in daylight, of course after pulverisation, very similar to ultramarine, but by artificial light its colour is a dirty violet. It is, however, not acted upon by acids, as distinguished from artificial ultramarine; neither is it affected by alkalies nor heat, as is copper or mineral blue. Cobalt ultramarine, chiefly under the denomination of Thénard's blue, is employed as a paint in oil- and water-colours, and also for staining glass and porcelain.

Cœruleum is a pigment prepared in England, exhibiting a bright blue colour, not changing in artificial light, and consisting of stannate of protoxide of cobalt (SnO_2,CoO), mixed with stannic acid and gypsum in the proportions, in 100 parts, of 49·6 of oxide of tin, 18·6 protoxide of cobalt, 31·8 gypsum. This pigment is not affected by heat, or the action of dilute acids and alkalies; nitric acid dissolves the protoxide of cobalt, leaving the other ingredients, from which the gypsum may be cleared by water.

Rinmann's, or Cobalt Green.—This substance, also known as cobalt green, zinc green, and Saxony green, is a compound similar to the cobalt ultramarine, for the alumina of which oxide of zinc is substituted. This green is prepared by mixing a solution of white vitriol with a solution of a salt of protoxide of cobalt, precipitating by carbonate of soda, and washing, drying, and heating the precipitate. This pigment

when pure contains 88 per cent. of oxide of zinc and 12 per cent. of protoxide of cobalt. It is not affected by strong heat, tinges the borax-bead blue, dissolves in warm hydrochloric acid, forming a blue colour, which, upon water being added, becomes a pale red. Treated with caustic potassa, the oxide of zinc is dissolved, and may be detected, after previous dilution with water, by the addition of a solution of sulphuret of potassium.

Pure Protoxide of Cobalt.—This substance is occasionally employed for the preparation of fine colours. It may be obtained by heating one part of previously roasted and finely pulverised cobalt ore with two parts of sulphate of potassa until no more sulphuric acid is given off. The fused mass, consisting of sulphate of potassa, sulphate of protoxide of cobalt, and insoluble arsenical salts, is, when cooled, first treated with water, and next digested with hydrated protoxide of cobalt to precipitate any iron which may happen to be present, and in order to eliminate the oxide of that metal the solution is filtered. It is next precipitated with carbonate of soda, and, finally, the precipitate is washed and heated.

Nitrite of Protoxide of Cobalt and Potassa.—This double salt, known by its trade name of cobalt yellow, is obtained by mixing a solution of protoxide of cobalt with nitrite of potassa; it is a yellow crystalline precipitate, perfectly insoluble in water. M. Saint-Evre first investigated this body, and, struck with its beautifully yellow colour, quite like that of *purrhee* (euxanthinate of magnesia), and with the fact that cobalt yellow resists oxidising and sulphuretting influences, suggested its applicability to artistic purposes. He prepares this pigment by precipitating with a slight excess of potassa the double salt of protoxide of cobalt and potassa, obtaining a rose-red-coloured protoxide of cobalt and potassa. Into this thickish magma deutoxide of nitrogen gas is passed. According to Hayes, this pigment is readily obtained by causing the vapours of hyponitric acid to pass into a solution of protonitrate of cobalt, to which some potassa has been added; the whole of the cobalt is then converted into cobalt yellow. As the nitrite of protoxide of cobalt and potassa can be obtained even from impure solutions of protoxide of cobalt, so as to be quite free from any nickel, iron, &c., the use of this preparation of cobalt is preferable for glass and porcelain staining when a pure blue is required.

Cobalt Bronze.—This substance, a double salt of phosphate of protoxide of cobalt and ammonia, prepared at Pfannenstiel, near Aue, in Saxony, has been but lately brought into commerce. It is a violet-coloured powder, very much like the violet-coloured chloride of chromium, and exhibits a strong metallic lustre.

NICKEL.

Nickel occurs in the following ores:—Kupfer nickel, NiAs, antimony nickel, NiSb, diosmose, $NiAs_3$, and especially in the nickeliferous varieties of speiss cobalt, nickel pyrites, NS, and nickel-antimony glance, $NiS_2 + Ni\,(SbAs_2)$. In New Caledonia occurs garnierite (pimelite or numeite), a nickel magnesium hydrosilicate (containing 11 to 16 per cent. of nickel), at present the most important ore of nickel. At Rewdansk, in the Ural, there is found rewdanskite, a hydrated nickelous silicate. Often magnetic pyrites and iron pyrites yield nickel, as does the cobalt-speiss of the blue colour works, and certain products obtained in copper works—*e.g.*, nickel vitriol—nickel is found in many kinds of pyrolusite and in some magnetic irons. It was formerly obtained in England from the residues of the chlorine stills. According to Gerland, 1 ton of pyrolusite yielded on an average 2·5 kilos. of nickel and 5 kilos. of cobalt.

A concentrative treatment has to precede the smelting of nickel ores. If nickel is present as a sulphide, iron pyrites are used for concentration; if the nickel is an arsenide, arsenic is employed. The product is in the former case matte, in the latter speiss. From these nickeliferous products metallic nickel or its alloy with copper is

obtained, either in the dry or the wet way. Hence the metallurgy of nickel is resolved into—

(I.) The concentration fusions, which aim at the accumulation of the nickel present in an ore, either (*a*) in matte, (*b*) in speiss, or (*c*) in black copper;

(II.) In the elimination of nickel or its alloy from the products of the concentration fusions, which may be effected in the dry or the wet way.

Since it has been understood that by preparing nickel-copper alloys the most valuable properties of nickel—its white colour and its resistance to chemical reagents—are masked, it is preferred to prepare pure nickel.

The concentration fusion of nickel ores is especially applicable if they occur among iron pyrites. The ferric oxide produced by smelting the partially roasted ores with quartz, or substances rich in silica, is chiefly slagged whilst the nickel, which is also oxidised, but which is more readily reduced than ferric oxide, becomes metallic, and collects in the matte formed from the undecomposed sulphides and the reduced sulphates. If the ore contains also copper, it concentrates in the matte more completely than does the nickel. If too much ferrous oxide is present, a part of it is reduced to metallic iron in contact with charcoal, and is either taken up in the matte or separates out as nickeliferous pig iron. An improved result is obtained if the matte is concentrated in a reverberatory with the addition of quartz, heavy spar, and charcoal, forming barium sulphide. This liberates baryta, and sulphurises the oxidised nickel and copper contained in the charge, whilst the baryta combines with the quartz and the ferrous oxide to form a very fusible slag.

At the Isabella Works at Dillenburg a nickeliferous sulphur and copper pyrites, containing on an average 7·5 per cent. ofnickel, is first roasted, broken up with coke, fused, roasted again, and finally smelted with the addition of slags, to form concentration matte. In order to diminish the iron and yet leave so much sulphur that the matte may be brittle and break easily, it is melted before the blast on the hearth, forming a refinery matte, from which nickel or a nickel alloy may be produced in the wet way.

The methods hitherto devised for obtaining nickel in the dry way have not given fully satisfactory results. In the wet way the first step is generally to roast the ores or the nickeliferous furnace products in order to convert the iron present into an iron oxide soluble in acids, and to render the nickel, copper, and cobalt soluble either in water, as sulphates, or in acids, as oxides or basic salts. From the solution the nickel is thrown down as oxide or as sulphide, and from the precipitate metallic nickel or the alloy of copper and nickel is obtained.

The wet process for nickel consists of—

(1) The preparation of the solution of nickel. If nickeliferous mattes are roasted, there are first formed the sulphates of the four metals iron, copper, nickel, and cobalt, which, at increasing temperatures, are decomposed at different degrees of heat: ferrous and ferric sulphate the most easily, and cobalt sulphate with the greatest difficulty. From the roasted mass the chief part of the nickel and cobalt are dissolved out in water, as is also a little copper, whilst the iron and a part of the copper with a little nickel and cobalt remain undissolved. From the residue, cuprous and nickelous oxides may be extracted by acids. If the roasted mass is at once treated with hydrochloric acid, copper oxide is dissolved rather than nickelous oxide, and nickelic and ferric oxides may be extracted from the residue by hot concentrated acids.

From speiss arsenic may be removed and the nickel dissolved by igniting the roasted speiss with a mixture of soda-saltpetre and soda, extracting the sodium arseniate with water, treating the residue with sulphuric acid, when nickel and cobalt sulphates are dissolved and ferric oxide is left. According to Wöhler's proposal, the arsenic can be removed as a sulpho-salt by melting the speiss with sodium sulphide and lixiviating the mass.

(2) The nickel is thrown down from the solution by fractionated precipitation with chalk, which separates first iron and arsenic and then copper, so that only nickel remains in solution, and is thrown down by means of milk of lime, free from iron. At Joachimsthal the copper is removed from the acid solution by means of sulphuretted hydrogen, the nickel is precipitated by potassium bisulphate in the state of sparingly soluble potassium nickel sulphate, when cobalt, free.from nickel, remains in solution, and can be thrown down by sodium carbonate.

(3) The conversion of the nickel precipitate into metallic nickel or copper nickel can be effected thus:—The hydrated nickelous oxide precipitated from the solution of the metal by lime-water is separated by filtration and pressing so that it may be dried. When dry, the precipitate is ground up with water, and washed with water containing hydrochloric acid until all gypsum is removed; the pure nickelous oxide stamped to a stiff paste with rye-meal and beetroot treacle,* and cut into cubes of 1·5 to 3 centimetres in diameter. These cubes are dried rapidly and reduced to metal by heating strongly in crucibles or upright fire-clay cylinders. This is easily effected in one and a half hour, but pure nickel requires three hours of an intense white heat. Since the introduction of galvano-nickeling, nickel is met with in commerce in ingots of great purity.

L. Mond has devised the following process for obtaining pure nickel. He finds that the liquid and volatile compound of Ni and oxide of carbon has not a corresponding Co compound. On passing the vapour of this liquid through a red-hot tube, the nickel is deposited alone.

The New Caledonian nickel ores which are now the chief material of the French nickel industry, consists of fine green hydrosilicates, and are free from arsenic and sulphur and poor in copper and cobalt. In consequence of the difficulty of working these ores in the dry way, Christofle treats them with hydrochloric acid, and precipitates the nickel alone as oxalate, which is calcined in crucibles. On account of the high price of oxalic acid, it is better to precipitate ferric oxide and alumina, and then nickel as oxide or sesqui-oxide, but the removal of the sulphuric acid, introduced along with the commercial hydrochloric acid, is difficult. The nickel thus obtained is very pure. Riche found in it 97·75 nickel, 1·25 carbon, 0·54 silicon, and 0·36 manganese. Subsequently Christofle has introduced a mixed process: he separates the ore as well as possible from ferric oxide in the wet way, and then reduces the purified ore in the dry way.

Samples of cast nickel have, according to Gard, the following composition:—

C	0·530	1·104	1·900
Si	0·303	0·130	0·255
Fe	0·464	0·108	0·301
Co	0.446	trace	trace
S	0·049	0·266	0·104
Ni	98·208	98·392	97·440
	100·000	100·000	100·000

Nickel is almost silver white, with a faint yellowish cast, very infusible, extensible, and capable of taking a polish. Its specific gravity is 8·97 to 9·26. When pure it may be forged, rolled, and drawn to wire. The tenacity of nickel to that of iron is as 9 to 7. It has a considerable resemblance to iron, but is distinguished by its greater resistance to chemical agents. Hence, it is suitable for crucibles and other laboratory implements. On account of its silvery colour and its resistance to the action of air, water, and many acids, it is used for the manufacture of alloys resembling silver. It is a constituent of the smaller coins in Germany, the United States, Brazil, &c. It serves also for coating other metals. Its porosity and crystalline texture, when melted on the large scale, can be removed by the addition of 0·1 per cent. of magnesium. At a white heat nickel may be welded with steel and iron.

* The latter article is not fit for human consumption.

COPPER.

Copper, one of the most common metals, was known in prehistorical ages.* The Greeks and Romans obtained this metal chiefly from Cyprus, whence the name cuprum. It occurs sometimes native, but more commonly as oxide and sulphide.

Copper Ores.—Metallic or native copper occurs in quantity near Lake Superior, where, in 1857, a mass was found weighing 450 tons, and measuring 13·75 metres in length, by 6·7 in breadth, and 2·7 in thickness. It is also found in Peru, Bolivia, and Chili, from which last country it is brought to England under the names of copper sand and copper barilla (!), containing 60 to 80 per cent. of copper, and 20 to 40 per cent. of quartz.

Red Copper Ore, ruberite, or ruby copper, Cu_2O, is found crystalline in regular octohedra as well as massive and diffused. It occurs in Cornwall and in large quantities in the Burraburra mine in South Australia.†

Tile ore is an intimate mixture of cuprous oxide with iron ochres.

Azurite (cuprazurite, copper lazulite, or azure malachite), $2CuCO_3.Cu(OH)_2$, is found in beautiful blue crystals as well as massive and diffused. It is found in Cornwall, at Chessy formerly, and in South Australia.

Malachite (a green copper carbonate), $CuCO_3.Cu(OH)_2$, occurs in oblique rhombic crystals, or stalactitic and fibrous (Atlas ore), or massive (copper green), generally mixed with azurite (Ural, South Australia, Canada).

Chalkosine (vitreous copper, copper glance), Cu_2S, and phillipsine, or purple pyrites, $3Cu_2S.Fe_2S_3$, and copper pyrites, $CuFeS_2$, are the most important sulphur compounds used for the extraction of copper. Copper pyrites is often accompanied with iron pyrites, arsenical pyrites, and fahl ore (grey copper), and also with silver, gold, and nickel.

Copper slate is a bituminous marly slate finely interspersed with sulphuretted copper ores. It occurs chiefly at Mansfeld, at Stollberg in the Hartz, and at Riechelsdorf in Hessia.

Enargite, Cu_3AsS_4, is found at Manilla, in Peru, and in Hungary.

The *Fahl ores* (grey copper) are composed of copper sulphide with silver sulphide, accompanied with arsenic and antimony sulphides. On account of the presence of silver, they often rank among silver ores. They contain 14 to 41·5 per cent. of copper.

Atakamite, $3Cu(OH)_2.CuCl_2$, contains 56 per cent. of copper. It is found in Chile and other parts of the west coast of South America, as also in South Australia, and is worked at Swansea. When ground to powder, it is brought from Peru under the name "arsenillo," and is used for sprinkling sand (to take up ink).

Several atakamites contain iodine as copper iodide. Since 1869 important quantities of copper have been obtained, in the wet way, from the burnt copper pyrites, the refuse of the sulphuric acid manufacture.

Copper is obtained from its ores either by the dry or the wet way.

In spite of concentration, it is rarely practicable to enrich copper ores so that they yield on smelting more than 8 to 10 per cent. of copper. Only pyritic ores are prepared by roasting. When the ores to be roasted consist essentially of copper pyrites, and are strongly contaminated with iron pyrites (sulphur ore), the attempt is made to utilise a part of the escaping sulphur, and to concentrate the copper (which often forms not more than 3 to 4 per cent. of the mixture) by means of *nucleus roasting*. If a mixture of sulphur ore with a little copper ore is roasted, the copper

* It seems to have been used for tools and weapons prior to bronze, and, of course, before iron.

† It is also found at Chessy, in France, along with copper carbonate, in the Bannat, and in Siberia in primitive rocks.

retires into the middle of the lumps, whilst the outer coating, which can easily be removed by mechanical means, consists of loose iron oxides very poor in copper.*

In certain cases the roasting is intended, not merely to expel sulphur, but to burn off the bitumen with which some ores are interpenetrated—*e.g.*, the bituminous copper shales. The fluxes in copper smelting are added, not only to make the charge more fusible, but to promote the separation of the iron from the copper oxide.

(A) *Production of Copper in the Dry Way.*—In pyritic ores this process is effected either in shaft furnaces or in reverberatories. In the latter the reduction of the copper oxide is effected by the sulphur itself. Thus the copper is more and more concentrated in the matte, until it is possible to proceed to the decomposition of the last portions of the sulphides. This decomposition is conducted by roasting the concentrated ore and its simultaneous smelting, whereon the air can have free access until the sulphur is entirely eliminated. There is then always a formation of cuprous oxide, so that the purified copper is in the state known as "overdone." In melting copper ores in shaft furnaces the same process is followed, of first concentrating the copper in a "copper matte;" but the reduction of the copper oxide after roasting is effected by means of charcoal, with which the charge of the shaft furnace is interstratified. In shaft furnaces the product is never overdone or contaminated with cuprous oxide, but always carboniferous copper. Consequently, malleable copper is obtained neither by means of the shaft furnace nor the reverberatory, but the means for rendering it fit to bear the hammer are completely different in the two cases.

The treatment of pyritic ores in shaft furnaces consists in roasting the ores, whereby a part of the sulphur, antimony, and arsenic is volatilised; a part of the metals present is converted into sulphates, arseniates, and antimoniates; whilst a part of the ore escapes roasting. In smelting the roasted mass with the addition of substances which form slag, the copper oxide is first converted to metallic copper; whilst the sulphates are again reduced to sulphides, which, with the metallic copper and the sulphides remaining undecomposed, form a richer crude matte (copper matte); whilst a speiss (antimonide and arsenide) is formed by the reduction of the existing metallic arseniates and antimoniates. The remaining metallic oxides, especially ferrous oxide, formed by reduction, combine with the fluxes to form slag.

By repeating the roasting and reducing processes there is ultimately obtained, along with a small quantity of matte, metallic copper (crude or black copper) contaminated with foreign metals, from which it is freed by an oxidising fusion, in which the foreign metals are partly volatilised as oxides and partly taken up in the slag. The finished copper (rosette copper, disc copper) contains, as the roasting process has generally been carried too far, cuprous oxide, by which its malleability is decreased. By a rapid reducing fusion, and by remelting upon a hearth between charcoal, the cuprous oxide is reduced, and there is formed malleable copper.

The crude smelting of the roasted ores to form crude matte (copper matte) is effected in cupola furnaces. Fig. 157 shows the section of the cupola furnace, and Fig. 158 its front elevation, with a removal of the front wall, to show the interior arrangements. Fig. 159 shows the interior of the furnace. Through the apertures, *t*, there pass the tuyères of the blast. The liquid contents of the furnace flow through the two apertures, *o* (eyes), situate above the sole, and two short channels into the two depressed basins, *C*. As the roasted copper ore always contains iron oxide, a simply reducing fusion might readily reduce the iron. To prevent this, substances capable of forming slag (quartz or silicates) are added, so that the iron oxide, when reduced to the ferrous state, combines with the silica present to yield a readily fusible slag.

* When the sulphur amounts to 30 per cent. or upwards, the ores should always be roasted in kilns, not merely to utilise the sulphur, but to obviate the nuisance of escaping sulphur dioxide.

The cupric and cuprous oxide formed are reduced to metallic copper by the iron sulphide present—($3CuO + FeS = SO_2 + FeO + 3Cu$).

During the formation of slag, sulphides separate out, and collect in the lower part

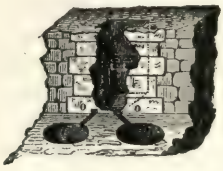
Fig. 157.



Fig. 158.



Fig. 159.



of the furnace as copper matte (crude matte), amixture of copper sulphide, iron sulphide, and other sulphides, containing on an average 32 per cent. of copper. The slag formed at the same time is the crude slag.

The roasting of the copper matte is to effect its complete oxidation and the removal of the sulphur present. The matter resulting is melted in a cupola furnace with an addition of slag, a process known as concentration work. The product is the concentration matte, containing about 50 per cent. of copper; it is thoroughly roasted off and melted to black copper. If silver is present this is extracted prior to any further treatment. This was effected formerly by amalgamation, but at present by the Ziervogel process (*see* SILVER), if it is not preferred to separate the silver from the copper by the eliquation process with lead.

In richer copper ores the concentration work is dispensed with, and the thoroughly roasted copper matte is smelted at once as black copper (crude copper, yellow copper). This takes place in cupola furnaces of less height than those used for smelting the roasted ores. The sulphur of the matte has been so much diminished by roasting that it can no longer take up the reduced copper. It separates out (along with a small quantity of matte) as black copper, with 93 to 95 per cent. of copper. Black copper from Mansfeld, according to Flach (1866), contained:—

Copper	93·49
Lead	1·49
Zinc	1·47
Iron	1·03
Nickel and Cobalt	1·25
Silver	0·03
Sulphur	0·99
	99·75

The black copper, or crude copper, is freed from impurities (sulphur and foreign metals) by a powerfully oxidising fusion, as the impurities are slagged more rapidly than the copper. This process—the finishing or cooking the black copper—is carried out (1) in a small finishing hearth, (2) in a large hearth or speiss-furnace, or (3) in a draught flame furnace or refining furnace.

The finishing hearth is shown in section in Fig. 160, and in elevation in Fig. 161. The hearth consists of masonry, on the upper surface of which is a hemispherical depression, *a*, the hearth-pit with a cast-iron covering plate, *b*. Black copper is melted down with the addition of charcoal, using the blast, *h*.

Sulphur, arsenic, and antimony are volatilised; ferric oxide and the other non-volatile oxides, along with cuprous oxide, separate out as slag in combination with silica from the mass of the hearth, and collect on the surface of the copper, where it is drawn off from time to time. When the copper is finished, the blast is turned off, the surface of

Fig. 160.

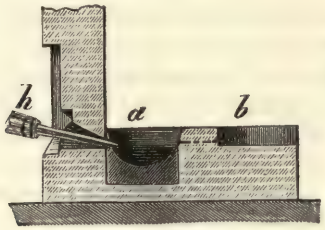
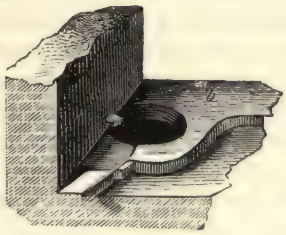
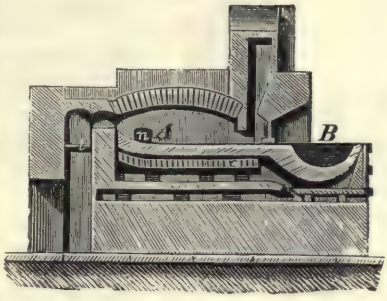


Fig. 161.



the copper freed from charcoal and slag, and cooled by sprinkling with small coal so far that it may be chilled superficially by means of water, without danger of an explosion. There is thus formed a thin disk (rosette), which is lifted off and immediately quenched in water to prevent the oxidation of the copper. Water is again sprinkled on, and another disc lifted off until the hearth is almost empty. This work is called rosetting, and the metal obtained is rosette, or disc-copper. This operation is better conducted in large blast-flame furnaces. The melting-hearth, *A* (Fig. 162), is provided with a fire-box, *l*, and apertures, *n*, for the blast. When it is finished, it is let off into the pan, *B*, and there converted into rosettes in the manner already described. As in this method the fuel is completely separated from the metal, the copper is more completely purified than in the small hearth.

Fig. 162.



Eliquation.—In working argentiferous copper ores, the black copper before refining is submitted to liquation, if it is not thought preferable to employ the Ziervogel method (*see* SILVER). This process depends on the principle that copper and lead may be fused together, but they do not remain combined on cooling. There is formed an alloy of much copper with little lead, whilst the remaining lead separates out. The separation takes place chiefly in accordance with specific gravity, the lowest stratum being argentiferous lead. If the liquid mass is allowed to cool slowly, the lead flows out in combination with the silver, but on rapid cooling there is formed an intimate mixture of both metals. The silver is separated from the lead either by the refining process, by Pattinson's process, or by means of zinc (*see* SILVER).

Copper, whether refined on a large or a small hearth, generally contains cuprous oxide. If this oxide is present to the extent of 1·1 per cent., the metal is so deficient in tenacity and malleability that it cannot be forged at common temperatures without splitting at the edges. If it contains 1·5 cuprous oxide the decrease of tenacity is perceptible, even when hot, and the copper is—both cold and hot—short. In this state it is said in Germany to be "overdone." Such copper contaminated with cuprous oxide can only recover its tenacity by the reduction of the oxide in order to become malleable.

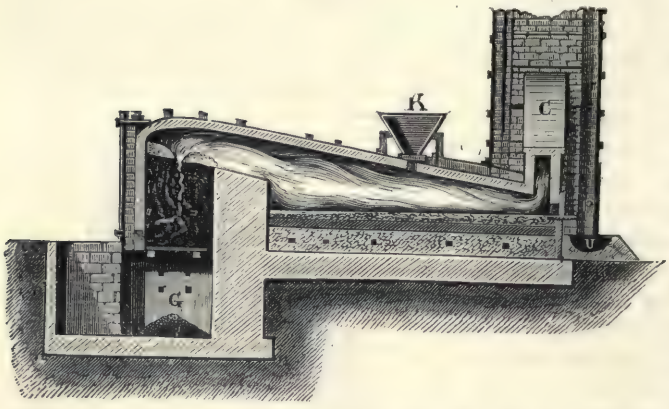
The great wealth of Britain in coal—the best fuel for the reverberatory process—probably first led to the idea of refining copper in reverberatories instead of shaft furnaces. The chief English copper-works are at Swansea; they obtain their ore from the mines of Cornwall, North Wales, Westmoreland, the adjoining parts of Lancashire and Cumberland; but very large quantities of ores imported from Australia, Chile, Peru,

Cuba, and Norway are also smelted. There are also copper works in Anglesea, Staffordshire, and South-west Lancashire. The English copper ores consist chiefly of copper pyrites accompanied by iron pyrites, also stannine and arsenical pyrites and gangue.

The chief processes of the English system of copper smelting consist of—(1) Calcining the pyritic copper ores; (2) melting the roasted ores for coarse metal; (3) roasting or calcining the coarse metal; (4) preparation of the concentrated white metal by melting the roasted coarse metal with richer ores; (5) preparation of the concentrated blue metal by melting the calcined coarse metal with calcined ores of a medium percentage of copper; (6) preparation of a red and white metal by smelting the slags obtained in the previous operations; (7) calcination fusion of the blue metal No. 5, and production of white extra-metal; (8) calcination fusion of the white extra-metal, and production of the concentrated metal; (9) calcination of the ordinary white metal and the cupriferous bottoms for the production of blister copper (black copper); (10) refining the blister copper.

The fusion of the calcined ores for coarse metal is conducted in the smelting furnace generally used at Swansea, and shown in Fig. 163. The hearth is contracted towards its mouth, forming a kind of tray. The object of smelting the coarse metal by the reverberatory process is the separation of the copper from the gangue, and from a part of the foreign metallic oxides contained in the roasted ore by means of a reducing and dissolving fusion. The sulphur is of importance, since the undecomposed sulphides during fusion decompose the oxides and the sulphates. Ferric oxide and iron sulphide are first converted into sulphur dioxide and ferrous oxide, the latter often combining with the silica present to form slag. As the heat rises the copper oxide is decomposed by the iron and copper sulphides with formation of ferric oxide and metallic copper, the latter of which partly dissolves in the coarse metal, and is partly converted by the ferric oxide into cuprous oxide, which becomes slagged at the highest temperature of the furnace. As the coarse metal and the slags are brought into intimate contact in the fused mass by means of constant stirring, the iron sulphide contained in the coarse metal and the cuprous oxide contained in the slags undergo a double decomposition into copper sulphide and ferrous silicate, so that the slagging of the copper is almost totally prevented.

Fig. 163.



The calcination of the coarse metal is mostly conducted in the same reverberatories which serve for calcining the ores. The purpose of this calcination or roasting is chiefly to oxidise the iron and to volatilise a part of the sulphur. A certain proportion of sulphur in the calcination products is necessary, since otherwise the concentration could not be effected without a loss of copper.

For the production of the concentrated white metal the roasted coarse metal is charged along with rich copper ores, which contain scarcely any iron sulphide, but copper sulphide, copper oxide, and quartz in such proportions that the iron pyrites is oxidised by the oxygen of the oxides, whilst all the copper coalesces to metal, and the iron oxidised to the ferrous state forms, with the quartz, ferrous silicate. The smelting

is conducted similarly to that of coarse metal. The concentrated white metal formed has almost the same composition as copper glance (Cu_2S), and is run off into moulds of sand.

The white metal is melted for blister copper. The metal is placed on the sole of a furnace, which does not differ from the smelting furnace, and the fire is allowed to act for twelve to twenty-four hours. At first the heat must not reach the melting-point, but it is raised towards the end. By this process the sulphur is removed in the state of sulphurous acid, and at the same time the impurities, such as arsenic, cobalt, nickel, tin, iron, &c., are removed either by volatilisation alone or by oxidation and slagging. Meantime the cuprous oxide and copper sulphide are mutually decomposed, forming sulphur dioxide and metallic copper ($2Cu_2O + Cu_2S = SO_2 + 6Cu$). The melted copper is run off into moulds, and is covered on the surface with black bubbles, whence its name, blister copper. The fracture has also a porous, honeycombed aspect. Blister copper is already moderately pure and almost free from sulphur, arsenic, and foreign metals. The last stage of the English process is refining the blister copper, which is effected on the sole of a reverberatory. The heat is gentle at first, to complete the oxidation. After about six hours the copper is in flux. When it has been all melted down into the sump, and the furnace is at a strong heat, the reddish slag, rich in cuprous oxide, is drawn off. The surface of the molten copper is covered with charcoal powder, and a wooden stirring rod, generally of birch, is thrust down into the liquid metal. The object of this operation—"poling"—is the reduction of the cuprous oxide by means of the gases evolved out of the cuprous oxide. The copper is then malleable.

For refining copper in the United States the native metal from Lake Superior is almost exclusively used in the three works at Hancock, Detroit, and Pittsburg. Pure copper and rich slag are obtained in a reverberatory. At Detroit and Hancock the refinery slags are worked up in shaft furnaces for blister copper and poor slags. The furnaces used at Lake Superior and Detroit, each for 10 tons of crude copper, are 4·3 metres in length; the fuel is Ohio coal, giving out a long flame. The slag, formed by smelting crude copper with cupriferous slags and limestone, containing mostly from 5 to 14 per cent. of copper, is drawn out four to six times, and finally freed from copper in a reverberatory or a shaft furnace. Five slags from Pittsburg had the following composition:—

	I.	II.	III.	IV.	V.
Cu_2O	12·46	11·43	12·01	12·02	10·53
Cu	4·82	4·93	5·05	5·80	5·44
O in Cu	1·22	1·24	1·28	1·46	1·37
Zn	0·37	0·56	1·52	0·75	0·43
Ni	0·06	—	0·47	0·18	0·08
MnO	0·05	0·04	0·15	0·13	0·12
Al_2O_3	15·71	14·52	15·21	14·48	15·36
CaO	14·34	14·75	14·79	15·25	11·81
MgO	4·07	3·99	4·11	3·90	2·57
SiO_2	45·32	46·94	45·81	44·66	49·83
	100·42	98·40	100·40	98·23	97·54

The copper now contains about 0·72 per cent. of oxygen. It is further heated with access of air through the arch, through the ash-door and the furnace bridge, and it is constantly stirred. The slags produced, containing from 12 to 40 per cent. of copper, are drawn off from time to time in order to add them to the next charge along with the finery slags, until the copper is overdone, containing about 1 per cent. of oxygen. It is now refined by means of poling, for the removal of the oxygen, the surface of the metal being entirely cleared from slag, covered with charcoal and split wood, and the pole introduced. Samples are taken every ten or fifteen minutes until black spots are

no longer seen upon the fracture, which becomes fibrous and of a silky lustre. At some works there is added during the refining 0·05 to 0·07 of lead, especially if the copper is to be wrought into sheets, and the pole is then introduced as soon as the lead distributed over the surface is melted. The poling is effected at the highest possible temperature, and with the greatest possible exclusion of air. Over-poling renders the copper brittle, light yellow, very shining, and mirror-like. Over-poled copper, apparently containing carbon, still retains oxygen. In presence of much carbon and oxygen there is formed carbon dioxide, which renders the copper porous. The withdrawal of the copper (which is to be kept covered with charcoal) is effected with a flame as neutral as possible, samples being frequently taken.

Manhés has carried out Holvay's proposal to work copper ores in the Bessemer converter. The furnace consists essentially of a horizontal cylinder of sheet iron, *A* (Figs. 164 and 165), lined with fire-proof stones acid or basic, which can be made to revolve on its axis by means of rollers. The external apertures, *c*, of the wind-chest, *d*, are opposite to the air-pipes, *e*, and can be closed with plugs. At *F* there enters the flame, which may be supplied from any kind of a fire-box, whilst the products of com-

Fig. 164.

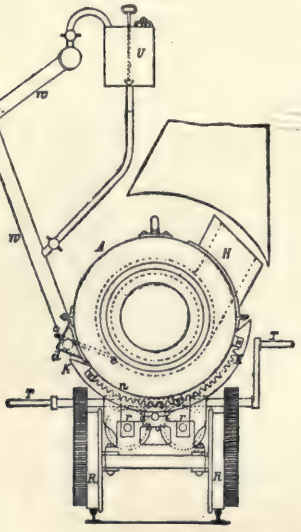


Fig. 165.

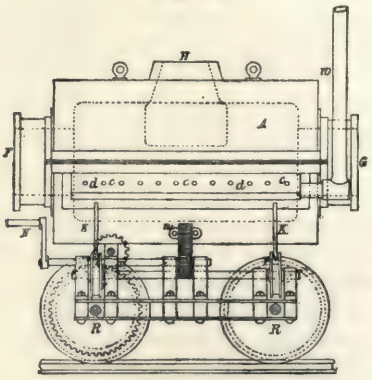
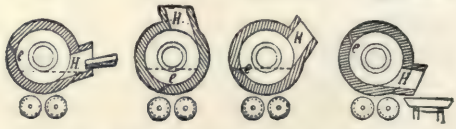


Fig. 166. Fig. 167. Fig. 168. Fig. 169.



bustion escape at *G*. When the apparatus is sufficiently heated it is brought up to the furnace containing the melted ore, the cylinder is turned (the arched pieces, *K*, lying upon the rollers, *r*) by means of the handle, *N*, which catches into the circle of teeth, *n*, fixed to the cylinder, until *A* takes the position shown in Fig. 166, and allows the melted metal to run to the mouth, *H*. It may also be baled in with a ladle, or the fusion may be effected in the cylinder itself by means of the flame striking in laterally. After the apparatus is sufficiently filled it is removed to a fit place by turning the wheels, *R*, which run on rails; the wind-chest is filled with compressed air or gas, and the cylinder, *A*, is placed in a proper position (Figs. 167 and 168). According to the action intended, the air flue, *w*, is connected with the recipient, *U*, so that the powdery substances which it contains may be blown into the liquid mass. By suitably inclining the melting furnace the slag, and afterwards the metal, can be run off (Fig. 169).

For working crude regulus, it is run into the heated cylinder, *A*, from an ordinary fixed smelting furnace; the cylinder is moved to the proper place and turned until the current of air passes through a sufficiently thick stratum of the liquid mass. The

oxygen of the air combines with the sulphur, forming sulphurous acid; and with the other substances, forming oxides, which are carried with the gases to condensation chambers, and are there precipitated. The sulphurous acid can be passed to the lead chambers and converted into sulphuric acid. Of the ferric oxide formed, the greater part remains in the bath, and would soon make the stone lining useless if silica were not constantly blown in. Therefore, when the current of air begins, the recipient, *U*, filled with silica, is connected with the air-pipe. As the more oxidisable substances escape first, there remains in the cylinder only copper sub-sulphide, which may be plainly seen by the colour of the flame. The cylinder is then turned so that the air is caused to play more and more on the surface of the metals. From this moment the copper is in excess—as the sulphur is continually being burnt—and separates out from the combination. The copper, by reason of its superior density, sinks down below the remaining copper sub-sulphide, and the tuyères are gradually so raised that the air only enters this sub-sulphide, which is thus gradually decomposed. There now remains in the cylinder merely crude copper, which is run out or can serve for refining copper in the ordinary manner. If the temperature is no longer sufficient, the cylinder may be heated afresh. If it is noticed during working that all the iron is oxidised, no more silica is blown in. The cylinder is turned to the position, Fig. 166, and the slag, if sufficiently liquid, is run out. The current of air which then strikes the back of the bath on the surface drives out the slag. With this apparatus very poor ores can be worked up, and refined copper can be obtained.

For producing copper from oxidised ores, they are smelted down with coke in a cupola furnace, after the addition of the fluxes necessary to produce an easily fusible slag which takes up no copper. The blister copper is then refined, and is introduced in commerce as rosette copper. At Chessy, near Lyon, malachite, azurite, and ruberite are smelted. There is, however, a considerable loss of copper by slagging. In the Siberian works on the Ural, sulphuretted copper ores and iron pyrites are added to the oxidised copper ores. The copper is thus protected from slagging by the sulphur.

(B) *Production of Copper in the Wet Way.*—This process is coming more and more into use. The great ease with which copper is dissolved and precipitated from its solutions suggested the moist way for obtaining copper when the dry way gave no advantageous results on account of the poverty of the ores, or when it was desired to utilise intermediate metallurgical and chemical products.

Cementation consists in precipitating copper from solutions of copper sulphate (blue vitriol, blue stone) by means of metallic iron. Such waters occur in nature in cupriferous districts. The metallic copper obtained by precipitating such solutions with iron is known as cement copper. At the Amlwch copper works in Anglesea the cement water is stored first in a large tank, to become clarified by the deposit of iron ochre, and is then run into the cement pits, in which has been placed scrap-iron, &c., for the decomposition of the copper sulphate. From time to time the sediments are stirred up, and the turbid liquor, with all the deposit, is led into large sumps, in which the mud is deposited and dried in a reverberatory drying furnace. It contains as much as 50 per cent. of copper—on an average 30 per cent.—the chief constituent being basic ferric sulphate.

Latterly the wet way for obtaining copper has been extensively used for the treatment of poor ochre and pyritic copper ores, weathered pyrites, and burnt ores containing copper pyrites. In general, the copper cannot be at once extracted by water or acids from ores and furnace products, but preparatory operations are needed. In cupriferous sulphur ores we use weathering or roasting (both oxidising and chlorising). The ores to be extracted are sometimes sulphated by means of roasting-gases. For lixiviation there are used, besides water, dilute hydrochloric or sulphuric acid, solutions of ferric and ferrous chloride, and of common salt. Other solvents, such as ammonia, sodium

sulphite, and thiosulphate, have not given satisfaction. The precipitation of the copper from its solutions is effected either by iron, or, as in Norway (Sinding's process), by sulphuretted hydrogen, the precipitated sulphide being afterwards converted into copper sulphate or metallic copper.

Cupreous pyrites (as at Duisburg), after having given off their sulphurous acid by roasting (for the manufacture of sulphuric acid), are freed from copper and silver in the moist way; the copper may be extracted by a solution of iron chloride and the copper precipitated with iron sulphide.

In the Dötsch process (worked at Rio Tinto) the pyrites are treated with ferric chloride: $CuS + Fe_2Cl_6 = 2FeCl_2 + CuCl_2 + S$ and $Cu_2S + Fe_2Cl_6 = 2FeCl_2 + Cu_2Cl_2 + S$. The practical utility of these reactions is that the ferric chloride in solution preferably attacks the cuprous sulphides, whilst the iron pyrites remain almost unchanged. Instead of ferric chloride there may be used a solution of ferric sulphate and common salt, which is distributed uniformly over the tops of the heaps. The solution penetrates downwards and runs into a tank, where it settles, and is next led into the precipitating tank. Before making up the heaps, 0·5 per cent. of common salt and an equal quantity of ferric sulphate are mixed with the pyrites. The height of the heaps varies from 4 to 5 metres. By means of methodic lixiviation 1·34 per cent. of copper, that is, the half of the 2·68 per cent. originally present, can be removed in four months; in two years, 2·2 per cent.; whilst by the old process of roasting in free heaps and lixiviation with pure water only, 1·1 per cent. can be obtained in the same time. The cuprous chloride is precipitated with iron; the lye is treated with chlorine and used afresh. The chlorine is obtained by igniting a mixture of sea-salt and iron sulphate with access of air: $2FeSO_4 + 4NaCl + 3O = Fe_2O_3 + 2Na_2SO_4 + 4Cl$.

An average sample of cement copper obtained by the Witkowitz Mining and Metallurgical Company, from the lixiviation of burnt ore, and also the crude copper obtained by melting it in crucibles without additions, had, according to L. Schneider (1884), the following composition:—

Cement Copper.

Copper	11·30 per cent.	Ferrous chloride	0·16 per cent.
Silver	0·521	Cobaltous chloride	0·29
Gold	trace	Nickelous chloride	0·07
Cuprous oxide	65·31	Arsenious chloride	1·32
Bismuth oxide	0·19	Lead sulphate	2·19
Iron oxide	3·86	Sodium sulphate	3·39
Zinc oxide	0·45	Calcium sulphate	5·32
Arsenious acid	1·18	Magnesium sulphate	0·59
Phosphoric acid	0·20	Water	2·98
Cuprous chloride	0·32		

Crude Copper.

Copper	92·752 per cent.	Cobalt	0·178 per cent.
Silver	0·699	Nickel	0·051
Gold	0·001	Zinc	traces
Arsenic	1·452	Phosphorus	0·055
Bismuth	0·188	Sulphur	0·190
Lead	0·760	Oxygen	0·360
Iron	3.111		

All cement copper, in consequence of the treatment with iron, contains generally considerable admixtures of basic ferric salts, which delay the refining, and occasion a loss of copper, if chlorine is present. For the removal of these salts there is required a mechanical preparation by washing, so that the proportion of copper is raised to 94·05 or 95·93 There may besides be present, iron, antimony, arsenic, lead, nickel, cobalt, lime, sulphuric acid, and chlorine (the last from 0·06 to 0·21 per cent.). Blister copper, obtained chiefly from rich ores, contained in three samples 87·02 to

94·31 copper, besides iron, antimony, arsenic, lead, nickel, cobalt, silver, and sulphur —the last from 1·06 to 2·11 per cent. Cement copper may be combined with lime to promote the formation of slag and to render the chlorine harmless.

The fusion with a reducing flame (the lateral draughts being closed), for the purpose of volatilising antimony and arsenic, lasts from nine to fourteen hours, according to the quality ; the treatment is then continued with open draughts, in order to slag the foreign materials, producing either a thinly fusible slag (cement copper after treatment with lime), or a basic, and merely fritted slag, containing iron and nickel, along with which there appears, if the mass in fusion contains arsenic, antimony or lead. A slag consists of nickel and lead antimoniates or arseniates, until a sufficiency of cuprous oxide has been formed, and this in the period of reaction is decomposed with copper sulphide, accompanied with strong effervescence (copper-rain) occasioned by the escape of sulphurous acid, as follows : $Cu_2S + 2Cu_2O = 6Cu + SO_2$. When the frothing and bubbling of the bath have ceased, the copper is more or less pure, but still contains antimoniates and arseniates in such quantity that a purification with soda is advisable for their removal, until a sample of the copper shows a crystalline fracture and a deep red colour. The copper then contains cuprous oxide, is overdone and porous, in consequence of sulphurous acid, which is still retained. Samples taken a short time before the apparent completion of the period of reaction have an earthy, very porous fracture, often of a greenish grey colour. After oxidation for some hours, and after the still existing impurities have become slagged, the fracture is densely earthy and red ; on further oxidation, corresponding to a proportion of 0·7 to 1·0 per cent. of oxygen, it is crystalline and deep red.

Poling then follows to expel the gas until the samples taken have the required compactness, shown by a finely earthy fracture. To render the copper ductile, the oxygen is expelled by means of tough poling, the metallic bath being covered with charcoal, with the draughts closed, and poled until the metal has a pure green colour, and samples taken have a silky lustre at the fracture, can be forged at a red heat without cracking, and at common temperature admit of stretching, bending, and twisting, and have a fibrous fracture. Lots containing bismuth and lead must not be over-poled, lest they entirely lose their oxygen, but only until a sample is sufficiently tenacious to be used for common sheet-copper. After the metal has become malleable, it is baled out, with iron ladles coated with clay, into moulds of iron or copper coated with clay ; samples are often taken, and the poling is regulated accordingly. If the poling gases (hydrogen and carbon monoxide) do not meet with sufficient oxygen for combustion they may be absorbed by the copper, rendering it porous and unfit for mechanical treatment. To prevent this absorption, especially in the case of copper free from bismuth and lead, red phosphorus wrapped up in thin sheet-copper has been used with success. According to Stahl, the phosphorus is best added to each lot of copper poured into the mould. On examining the following refined coppers—

	I.	II.	III.	IV.
Cu	99·365	99·842	99·778	99·662
As	0·466	0·052	0·004	0·066
Sb	trace	—	—	0·028
Fe	0·004	0·001	0·002	0·002
Ni	0·016	0·004	0·001	trace
Co	0·034	0·008	0·003	trace
O	0·050	0·062	0·206	0·042
S	0·001	—	—	—
Pb	0·015	trace	trace	0·043
Sn	0·008	—	—	Bismuth 0·102
Au	—	0·004	—	—
	99·959	99·973	99·994	99·945
Sp gr.	8·904	8·488	8·908	8·468

the arseniferous copper I. was tougher than II. and III.; the latter not tougher than at common temperature, but in a red heat more easily forged and rolled than II.; IV. was both hot and cold short. This behaviour shows that corresponding quantities of arsenic prevent the absorption of the poling gases, and thus give a denser copper, which is tougher than the porous qualities, because the molecules remain more united, and the intervening substances, in this case arsenic, in the quantities present do not exert an injurious effect upon the properties of the copper. Whilst II., on account of its larger percentage of copper and oxygen, might lead us to expect a higher degree of toughness, its lower sp. gr. indicates porosity, whence the copper is in reality less tough than II. The high precentage of copper and the considerable density of III. render it fit to be forged and rolled at a red heat, but its proportion of oxygen is enough to render it cold short on working at a common temperature. IV. is both hot and cold short, on account of the presence of metallic bismuth.

In general, the coppers treated during refining for the partial removal of oxygen with phosphorus, manganese, phosphide, &c., prove tougher and firmer than such as have been poled tough. At the conclusion of the dense-poling, the copper contains about 0·2 per cent. of oxygen, which allows it to be rolled and forged at a red heat, but not at common temperatures. If an attempt is made to reduce the oxygen to 0·07 or 0·05 by continuous tough poling, in order to get rid of the cold shortness, the metal absorbs pole gases to such an extent that it fulfils the required conditions even less by its porosity than by the former presence of oxygen. Melted copper dissolves gases (sulphur dioxide, hydrogen, and carbon monoxide), which are expelled by carbon dioxide. At the Olper Works a sample of copper purposely over-poled was converted into a very dense and tough copper by passing into it a current of carbon dioxide. The absorption of gases involves the so-called rising or running of the copper. Böttcher has found the cause of his phenomenon to be the absorption of sulphurous acid into refined copper. As the copper cools, the gas becomes liberated again. It is formed by the action of copper sulphide upon cuprous oxide: $2Cu_2O + Cu_2S = 3Cu_2 + So_2$.

Whilst, according to Ledebur, with the decrease of copper sulphide and cuprous oxide in the metal-bath, the transformation of these substances is proportionately retarded, Hampe shows that, in spite of the presence of oxygen, copper may contain copper sulphide and sulphurous acid.

Three Mansfeld coppers had, *e.g.*, the following composition:—

	I.	II.	III.
Cu	98·9048	99·5200	99·6125
Ag	0·0287	0·0280	0·0292
Pb	0·0208	0·0232	0·0200
As	0·0223	0·0228	0·0172
Sb	0·0059	0·0031	0·0023
Ni	0·2200	0·2142	0·2112
Fe	0·0029	0·0039	0·0039
O	0·7464	0·1546	0·0752
S	0·0036	0·0021	0·0024
	99·9627	99·9719	99·9739

I. is overdone copper, after nine hours' melting and four hours' poling; II., dense refined copper after dense-poling for one and a half hour; III., refined copper after tough poling for one hour.

If the quantity of copper sulphide is sufficiently small it cannot be detected during dense poling in the ladle samples, because a sufficiency of oxygen for transformation and for the formation of sulphuric acid is wanting. It passes through the stage of tough poling, and finally comes to be cast, but meets here with the newly formed cuprous oxide, and forms with it sulphurous acid, which occasions the rising of the copper. This

behaviour occurs if the dense poling stage is begun at that point which is indicated by samples with a dense earthy fracture, since the proportion of oxide at this stage is mostly not sufficient for conversion with all the copper sulphide, however uniformly the particles are mixed by the poling, along with the demands of the reducing gases. If, on the contrary, the dense poling has been begun at the point characterised by a crystalline fracture, the proportion of oxygen of the cuprous oxide, which is formed more abundantly, suffices for complete conversion with the copper sulphide; and the copper does not rise on casting, if this is not produced by pole-gases or by sulphurous acid evolved from pyritic fuel, which were absorbed by the copper after tough poling. This may be ascertained by a sample before casting. That it is not always sulphurous acid which occasions the rising of the copper, but that this phenomenon may be due to the pole-gases (hydrocarbons, carbon monoxide, hydrogen), is proved by the fact that even the best coppers, smelted with the best fuel, rise the more the longer the period of toughening lasts. Stahl has shown that there was no trace of sulphur in some highly-poled coppers which had risen. If the rising has been occasioned by sulphurous acid, sulphur is, as a rule, still demonstrable in the copper. It is very difficult, whilst ladling out the copper, to regulate the access of air so that all the combustible gases are burnt, whilst the copper remains unchanged. If the supply of air is too scanty, there is a reducing atmosphere in the furnace, the copper absorbs carbon monoxide, it becomes porous, and it must be again rendered dense by oxidation or by the method stated below. If the access of air is too free, the copper goes back, takes up oxygen, and must be again poled until it is tough. Combustion gases are not absorbed, since their ultimate products, carbon dioxide and watery vapour, are not absorbable.

The presence of oxygen, lead, arsenic, or phosphorus has a marked influence on the density of copper. As the proportion of oxygen decreases on poling from 0·210 to 0·051 per cent., the porosity of the copper increases by taking up pole-gases. With a proportion of oxygen of 0·160 per cent. the absorption of gases is just perceptible; but lower down it becomes very distinct, and as the oxidation of the copper increases its density follows. An absorption of the gases makes itself perceived before the proportion of oxygen has been reduced by tough poling as far as necessary for producing sufficient toughness, and if the period of tough poling is too much prolonged the gas-absorption goes to such an extent that the copper is worse than when it contained from 0·200 to 0·160 per cent. of oxygen.

The addition of lead is said to prevent the rising of copper from sulphurous acid, becoming converted by the acid into lead sulphide and lead oxide, and also to render the copper fitter for forging and rolling, by purifying it from antimony and arsenic. According to Stahl, it condenses porous copper by dissolving therein, becoming partly evaporated, and expelling the gases, just as do watery vapour and carbon dioxide. An excess of lead added in refining makes the copper exfoliate on rolling. Under certain circumstances arsenic prevents the absorption of the pole-gases and keeps the copper dense. Such arseniferous copper, obtained even after prolonged poling, has, along with a low proportion of oxygen, the property of being better adapted for working than less dense refined copper richer in oxygen, even up to a proportion of arsenic of 1 per cent. Antimony acts similarly to arsenic. In copper free from lead and bismuth, phosphorus, as a reducing agent, acts favourably upon the density of copper. The porosity of copper occasioned by sulphurous acid or pole-gases is distinct from that which arises during casting, by air bubbles carried along mechanically.

Obtaining and Refining Copper by Electricity.—The installation erected by Marchese for a company at Genoa consists of 20 Siemens machines for electrolysis, each of which, with a tension of 15 volts and a current of 250 ampères, serves 12 baths. A part of the ores to be treated are smelted, according to their nature, to a raw matte, which serves in the process as an anode (positive pole), and consists of about

30 per cent. copper, 30 sulphur, and 40 iron. Another portion of the ores is roasted to produce a liquor containing as much copper sulphate as is necessary to utilise the iron sulphate of the anodes for the electrolytic decomposition of the same solution of copper sulphate. That part of the mineral which is reserved for anodes is melted to raw metal in the ordinary manner. The crude metal is cast in thin plates corresponding to the sizes of the troughs, and into each there is inserted a slip of copper to effect the connection with the circuit. The kathodes (negative poles) are formed of thin sheets of copper. The roasted ores are systematically lixiviated with the addition of sulphuric acid, in order to dissolve the metal present as oxide, and the solution obtained, a mixture of copper and iron sulphate, is passed into cisterns. Copper sulphate is decomposed by the electric current, the copper being deposited upon the kathodes; at the same time the metallic sulphates forming the anodes are attacked; there are formed iron salts and sulphuric acid, which prevent the precipitation of iron from the copperas (iron sulphate) and the development of hydrogen. In order to keep the solution saturated and of correct composition, it is passed through the collecting pipes from the separate baths to the cisterns for liquor, and thus a regular and constant circulation is maintained between the baths and the cisterns. The tension required is about one volt. The worn-out anodes are utilised for sulphur or sulphuric acid. If the solution contains too much iron it is removed; the last traces of copper are precipitated by the sulphuretted hydrogen evolved by the action of the liquor upon the raw metal. In the same manner, the ferrous sulphate is reduced and the free sulphuric acid is neutralised. The ferrous sulphate is crystallised out, if it is saleable, by a suitable arrangement of the baths, a proper composition of the solution, and a well-managed circulation; the daily yield of pure copper is said to be 20 kilos. per horse-power.

The diagram (Fig. 170) makes the succession of the operations more intelligible.

Siemens and Halske use as depolarising agent a liquid in connection with insoluble anodes, and separate the salt of copper to be decomposed at the kathode from the liquid to be oxidised at the anode of a non-metallic septum. The liquid submitted to electrolysis consists of a solution of iron and copper sulphates, with the addition of some free sulphuric acid to increase its conductivity.

If single decomposition cells are used, this liquid is best introduced, without interruption, near the bottom of the solution surrounding the kathode plates (Fig. 171); it rises here whilst a part of the copper is deposited by the electric current at the kathodes, *Cu*, and flows over the upper edge of the membrane, *C*, into the anode-spaces, which it traverses in order to be drawn off again at the bottom, through *Ra*.

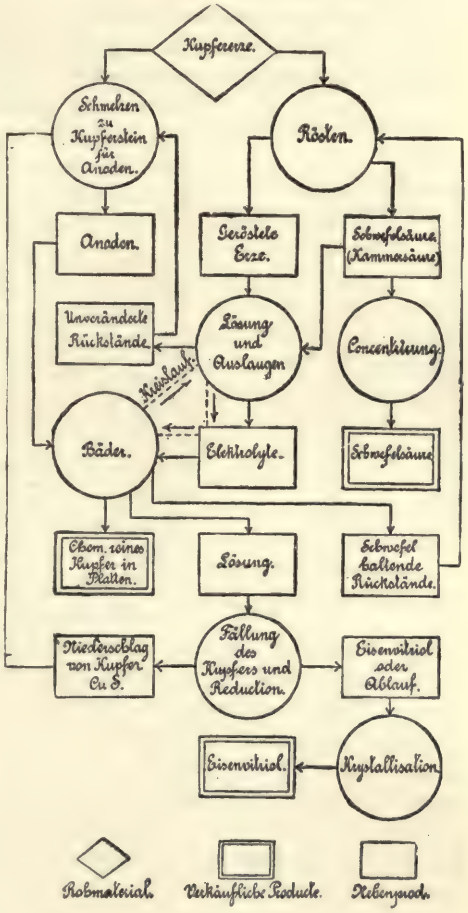
During this descent the ferrous sulphate is first decomposed into basic ferric sulphate, and then, by taking up the sulphuric acid liberated in the decomposition of the copper sulphate, it is converted into neutral ferric sulphate, which, on account of its greater specific gravity, sinks to the bottom at the carbon rods or plates. The liquid flowing off has therefore become poorer in copper and consists in part of neutral ferric sulphate. This solution has the property of converting copper sub-sulphide, copper mono-sulphide and copper oxide into copper sulphate. Hence, by the solution of the two copper compounds, the ferric sulphate is reconverted into ferrous sulphate, whilst the oxygen liberated oxidises the copper sulphide. By previously roasting the copper pyrites at a gentle heat, a product has been obtained in which the copper exists chiefly as copper hemi-sulphide and the iron as oxide, the latter, therefore, in a state in which it is not attacked by ferric sulphate and very slightly by sulphuric acid, whilst the copper hemi-sulphide is powerfully dissolved by the solution of ferric sulphate.

The process is continuous, the same liquid serving until it is rendered unfit for galvano-deposition, by having taken up foreign metals.

The chemical processes involved appear from the following equations :—

1. $xH_2SO_4 + 2CuSO_4 + 4FeSO_4 = 2Cu + 2Fe_2(SO_4)_3 + xH_2SO_4$.
2. *a*. $xH_2SO_4 + Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + xH_2SO_4$.
 b. $CuO + H_2SO_4 = CuSO_4 + H_2O$.
 c. $3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3$.
 d. $CuO + 2FeSO_4 + H_2O = CuSO_4 + (Fe_2O_3 + SO_3) + H_2$.

Fig. 170.



Explanation of Terms.

Kupfererze	Copper ores.
Schmelzen zu Kupferstein für Anoden	Fusion to copper matte for anodes.
Rösten	Roasting.
Anoden	Anodes.
Geröstete Erze	Roasted ores.
Kammersäure	Chamber acid.
Unverandecte Rückstände	Unchanged residues.
Lösung und Auslaugen	Solution and Lixiviation.
Concentrirung	Concentration.
Kreislauf	Circulation.
Bäder	Baths.
Elektrolyte	Electrolyte.
Schwefelsäure	Sulphuric acid.
Chemisch. reines Kupfer in Platten	Chemically pure copper in plates.
Lösung	Solution.
Schwefel haltende Rückstände	Sulphurous residues.
Niederschlag von Kupfer, CuS.	Precipitate of copper, CuS.
Fällung des Kupfers und Reduction	Precipitation of copper and reduction.
Eisenvitriol oder Ablauf	Copperas or waste liquor.
Eisenvitriol	Copperas.
Krystallisation	Crystallisation.
Rohmaterial	Raw material.
Verkäufliche Producte	Saleable products.
Nebenproducte	Bye-products.

On comparing the formulæ 1, and 2 *a*, we perceive that if the ore contains all its copper in the form of a hemi-sulphide the electrolyte contains, after the transflux of the lixivium, exactly the same quantity of copper sulphate, iron sulphate, and sulphuric acid as before electrolysis, and is therefore completely regenerated and can be again used for electrolysis. If, on the contrary, the copper is partly present in the ore as oxide, it is seen from equations 2 *b*, *c*, and *d* that in this case after lixiviation the electrolyte is richer in copper but poorer in iron than it was before electrolysis.

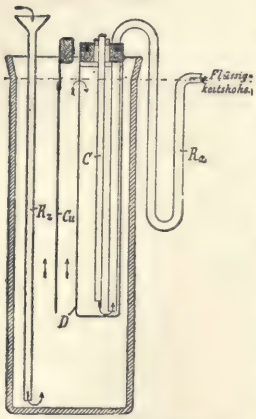
It need scarcely be mentioned that, instead of roasted copper pyrites, unroasted raw matte in which the copper is almost exclusively present as hemi-sulphide may serve for lixiviation. Here not only copper, but iron, is dissolved, so that a complete uniformity of the solution in copper and iron is not reached.

In the galvanic process described, no polarisation occurs, and the different position of the anode and kathode in the series of tension does not occasion any counter electric force.

Whilst, on using anodes of raw metal, there is required a potential difference of about 1·5 volt in the processes above described, there is needed a tension of only 0·7 volt for the same density of current. Whilst, further, in using anodes of copper matte, about one-third of the current is used in other reductions and is consequently wasted, there is here no loss of current.

For refining copper the distance of the electrodes is 5 centimetres, the density of the current is 20 to 30 ampères per square metre of kathode surface, and the bath is a solution of 150 grammes copper sulphate and 50 grammes sulphuric acid to 1 litre water. The tension for the bath is 0·1 to 0·2 volt. Manganese, zinc, iron, cadmium, tin, antimony, arsenic, lead, and bismuth pass into the liquid, remaining in the mud at the anodes only if insoluble compounds are formed. Silver, platinum, and gold are deposited on the anode in the metallic state. It is essential that the bath must remain acid and must be kept constantly in motion.

Fig. 171.



Explanation of Terms.

Flüssigkeitshöhe—Level of liquid.

If the tension at the terminals of the dynamo is 15 volts, the tension in the bath 0·25 we might put $(15 : 0{\cdot}25) = 60$ baths in series. For the sake of safety, 40 are used. If the dynamo yields 240 ampères hourly, corresponding to 283·6 grammes copper, we obtain in twenty-four hours in 40 baths, arranged in series, 272 kilos. The work required is $(240 \times 15) : 736 = 4{\cdot}9$ horse-power in the dynamo or 6 horse-power in the engine. If the tension in the bath, using plates of very impure copper matte, and impure solutions, is 1·2 volt, so that only 10 baths can be arranged in series, we obtain only one-fourth of the quantity of copper from the same machine-power.

At Oker there are now 6 dynamos in action, 5 of the type C_1 and one C_{18}, each of which daily deposits 250 to 300 kilos. of copper, with the expenditure of 7 to 8 horse-power. The yearly output is therefore 500 to 600 tons of copper. The copper to be refined has already undergone a furnace refining, and contains only $\frac{1}{3}$ to $\frac{1}{2}$ per cent. of impurity. Nevertheless, the electrolytic process is financially remunerative, as the removal of the last impurities considerably raises the value of the product.

The great advantage of the electrolytic process as compared with furnace-refining is, that the precious metals, especially silver, do not pass into solution, but, as the anode is gradually destroyed, they fall down into the mud. To obtain all the silver present in the crude material, it is merely necessary to remove from time to time the mud which collects, and to extract the silver. The greatest difficulty of the electrolytic process lies in the behaviour of arsenic and antimony. They pass into solution, and as soon as they exceed a certain proportion they begin to combine with the deposit of copper, and render it hard and brittle. In order to meet this difficulty there is no expedient except to purify the solution or to prepare a fresh solution in its stead. Both the crude copper and the refined copper are used in plates 1 metre in length and 0·5 metre in breadth. The plates of crude copper, about 15 millimetres in thickness, are fixed in boxes at the mutual distance of 10 to 15 centimetres, and plates of copper are inserted between them as kathodes.

Each dynamo C_1 with a tension at the terminals of 3·5 volts, and a current of 1000 ampères in strength, works, as a rule, 12 baths introduced in series, the whole occupying a space of 80 square metres. The dynamo C_{18} gives a tension of 30 volts and a current

of 120 ampères (or in other cases 15 volts and 240 ampères). It actuates at Oker 80 smaller baths. The room occupied, the quantity of liquor, the working-power, and the deposit of copper are in this case quite similar to the arrangements with C_1 dynamos. The expense, however, differs, and a decided advantage of the installation C_{18} is that the baths can be placed at a considerable distance from the machine, which is not the case with C_1.

Hilarion Roux, of Marseilles, has a 5 horse-power Gramme and 40 baths, with a surface of anodes = 900 square metres. The kathodes are only 0·5 millimetre in thickness, and are fixed at the distance of 5 centimetres from the anodes. The machine consumes daily 240 kilos. of coal and yields at 8 volts and 300 ampères 250 kilos. of purified copper or 10·4 kilos. hourly. The machine utilises 85 per cent. of the power supplied = 319 kilogrammetres; 240 of which, according to Gramme, are spent in overcoming resistance, and 79 in transporting the metal between the poles; chemical work has not here to be performed.

In order to calculate the necessary expenditure of work, the potential difference between both electrodes must be measured in a laboratory experiment, with that density of current which has been found most favourable for general working, and with the intended distances of the electrodes. If, *e.g.*, the tension at the terminals of the machine is 15 volts, and the tension at the bath 0·25 volt, we might, if we quite overlook the resistance of conduction outside the baths, at most introduce (15 : 0·25) = 60 baths in a series, but 40 are generally found sufficient. If the machine at the above tension gives a current of the strength of 240 ampères, representing 238·61 grammes copper hourly, we obtain in 40 baths arranged in series 11·344 kilos. hourly, or in twenty-four hours 272·26 kilos. of copper. The work consumed is (240 × 15) : 736 = 4·9 horse-power for a dynamo, or 6 horse-power for the steam-engine. Such an installation takes up a surface of 80 square metres, and five months are required for producing a copper plate of 1 centimetre in thickness, with a current of 20 ampères.

Properties of Copper.—Copper is red, strongly lustrous, and, though considerably hard, it is so ductile that it may be drawn out to very fine wires and rolled into thin leaf. It has a granular fracture, a spec. gr. (pure) of 8·955 to 8·956; the best commercial samples have only 8·2 to 8·5; it fuses rather less readily than silver. Pure copper flows in a thin stream, which quickly solidifies; if contaminated with cuprous oxide, it flows more sluggishly and solidifies less rapidly. Melted copper has a peculiar sea-green colour. For castings copper is not good, since it gives porous articles full of air-bubbles, probably because cast too hot. At high temperatures, and with access of air, copper burns with a fine green flame. If exposed to moist air, it gradually becomes coated with copper hydrocarbonate, commonly but improperly called verdigris. If heated with access of air, it takes at first rainbow colours, and then becomes covered with a reddish-brown film of cuprous oxide, which by degrees turns black, and on quenching the ignited metal in hot water, or on hammering or bending, falls off in scales.

Copper is used for boiling-vessels and coolers in distilleries, breweries, and sugar-works, for sheathing ships, for money, for rollers in tissue-printing, for making copper sulphate, nitrate, and copper colours, for engraving, and especially in the production of alloys. The *Mining Journal* estimates the quantity used yearly in cartridges at 7500 tons.

Among samples of refined copper examined in 1884 by Pupahl, two brands were found unsuitable for brass castings, on account of their high percentage of arsenic:—

	Wallaroo.	Chm. Co.	Mansfelder R.	Bede.	Grange.
Cu	99·795	99·864	99·491	99·148	98·961
O	0·127	0·120	0·145	0·090	0·160
Pb	0·004	—	0·038	0·023	0·005
Fe	0·001	trace	0·001	0·001	0·004
Ni	0·039	0·002	0·201	0·081	0·066
Ag	0·015	0·028	0·031	0·058	0·010
Au	—	trace	—	trace	—
S	—	—	—	0·005	trace
As	—	trace	0·072	0·600	0·766
Sb	—	—	trace	0·002	0·011
	99·981	100·014	99·979	100·008	99·983

Copper obtained from Colorado ores contains, according to Eggleston (1883), tellurium, which renders it brittle.

	Stone.	Black Copper.		Refined Copper.
Cu	55·02	97·120	98·090	99·705
Au	0·06	—	—	—
Ag	0·40	0·132	0·128	0·135
Pb	17·87	0·777	0·757	—
Zn & Ni	2·22	0·070	0·100	0·024
Fe	4·18	0·130	0·080	0·031
S	20·02	0·236	—	trace
Te	0·12	0·093	0·097	0·083
As	—	0·006	—	0·091
Slag	—	1·270	0·192	—

Refined Mansfeld copper (1880) contains:—

	A.	B.
Cu	99·394 to 99·550	99·110 to 99·270
Ag	0·028 „ 0·030	0·016 „ 0·020
Pb	0·043 „ 0·103	0·134 „ 0·259
Fe	0·025 „ 0·132	0·019 „ 0·024
Ni	0·239 „ 0·275	0·314 „ 0·405
As	—	0·101 „ 0·144

The total production of copper in 1879 amounted to 149,000 tons, and in 1884 to about 208,000 tons, of which the United States furnished 63,950, Chili 41,648, Spain and Portugal 43,664 (chiefly from Rio Tinto), Australia 13,300, South Africa 5000, and England only 2500.

Copper Alloys.—Among the copper alloys, the most important are bronze, brass, and nickel-silver, commonly called German silver. Bronze is an alloy of copper and tin, or copper, tin, and zinc; or, latterly, of copper and aluminium. By these additions copper is rendered more fusible, and hence easier to cast; denser, and thus more susceptible of polish, it is also harder, more brittle, sonorous, and resonant, and is (with the exception of the aluminium alloys) cheaper, and thus more suitable for a variety of purposes. Lead renders bronze more fusible and denser, but has a great disposition to separate out on the surface in combination with copper. Hence a percentage exceeding 3 per cent. is to be avoided. On slow cooling bronze becomes soft and malleable, but on rapid cooling hard and brittle. A small addition of phosphorus (0·12 to 0·76 per cent.) makes some of these alloys more homogeneous and pliable. The chief kinds of bronze are bell-metal, gun-metal, art-bronze, phosphor-bronze, and aluminium-bronze, the last of which will be described under ALUMINIUM.

Bell-Metal, of spec. gr. 8·368, consists of 78 parts copper and 22 parts tin. It must combine sonorousness with hardness and tenacity. It is a brittle metal, and its treatment in the turning-lathe is therefore difficult. A bell must obtain its intended sound in the casting, by its form and by its composition. It is an error to suppose

that silver has to be mixed with bell-metal to yield a good sound. The alloy for certain instruments of military music, such as cymbals, as well as of tom-toms and gongs, is similar to bell-metal.

Gun-Metal consists, on an average, of 90 parts copper and 9 tin. It has the defect of becoming gradually decomposed, either by a kind of eliquation, more fusible alloys richer in tin separating out from less fusible parts richer in copper, or by combustion, since tin burns more readily than copper, the alloy thus becoming poorer in tin.

Art-Bronze, for statues, busts, decorations, &c., consists of copper and tin. It must be so composed that when melted it fills up the mould completely, giving a clear, sharp casting, which admits of being easily retouched, and takes a fine patina. A normal bronze, according to Elster, consists of 86·6 copper, 6·6 tin, 3·3 lead, and 3·3 zinc.

Bronze is valued for its property of quickly becoming coated with a uniform fine green layer of oxide (patina), the formation of which is often expedited by chemical means. According to Weber, zinc hinders the formation of patina; he recommends that copper, as free as possible from arsenic, should be used with tin alone. A bronze statue having a remarkably fine patina consisted of 88·6 per cent. copper, 9·1 per cent. tin, 1·3 zinc, and 0·8 lead.*

Phosphor-Bronze (90 parts copper, 9 tin, and 0·5 to 0·75 phosphorus) was invented in 1871 by C. Künzel. It has been latterly used for gun-metal, bell-metal, art-bronze, for the bearings of axles, &c. The elasticity is considerably heightened and its absolute tenacity is increased more than twofold by the introduction of phosphorus, and the hardness is augmented to such a degree that some specimens resist the file. The metal when melted flows well and fills the mould perfectly.

Brass.—Zinc and copper combine with each other in all proportions, some of which are well known as brass, and find numerous applications. The following are instances:—

	Cu.	Zn.	Pb.	Sn.
Clock wheels	60·66	36.88	—	1·35
Cast brass	63·70	33·50	0·30	3·50
Sheet brass	70·10	29·90	—	—
Brass wire	71·89	27·63	0·85	—

In general, a reduction of the proportion of zinc gives the brass a darker and a redder colour; a larger proportion of zinc gives a paler and yellower metal. The larger the proportion of copper the more extensile is the brass. When cold, brass is malleable and can be rolled and drawn to wire. When hot, it easily breaks and cracks. A malleable brass (yellow metal) which can be forged and rolled is obtained by melting together 60 parts of copper with 40 of zinc.

Brass is superior to pure copper in several respects. It has a more pleasing colour, does not oxidise so readily, is harder and stiffer (whence its use for pins); has a lower melting-point, and when melted flows more easily and does not become blistery; hence, and from its lower cost, it is preferred for castings. The addition of 1 or 2 per cent. of lead makes the brass more suitable for turning; it also files better, and does not clog the file.

Brass was formerly manufactured by fusing together calamine with black copper and charcoal. Now it is produced by melting metallic zinc with refined copper.

Alloys similar to brass are pinchbeck (tombak), containing 85 parts copper with 15 zinc. Spurious gold-leaf is made in Germany from 2 parts zinc and 11 copper.

Other alloys are prince's metal, similor, oreïde, Mannheim gold, &c. Delta metal is composed of 60 parts copper, 32·2 zinc, and 1·8 iron. Sterro-metal is similar in

* The formation of patina is now found to be due to the action of certain minute organisms.—[EDITOR.]

composition, but much harder. Muntz's metal, used for sheathing ships, for bolts, ships' nails, &c., consists of copper and zinc in proportions fluctuating between 50 per cent. zinc to 63 copper and 37 zinc to 50 copper. The alloy for the bronze coinage of France, Sweden, Britain, Spain, Russia, Norway, Greece, Servia, and Roumania consists of 95 parts copper, 3·5 tin, and 1·5 zinc. In Denmark the alloy is 90 copper, 5 tin, and 5 zinc. The German bronze coins (2 and 1 pfennig pieces) consist of 95 copper, 4 tin, and 1 zinc. So-called white brass consists, like bath metal, of 55 copper and 45 zinc. Button metal is composed of 20 copper and 80 zinc.

The *Bronze colours* used for bronzing objects of plaster or wood, as also for cast-metal articles, in letter-press and lithographic printing, in lacquering, and in the manufacture of paper-hangings, &c., are made from the powders resulting from forging metals, which are ground up and heated with oil, tallow, wax, or paraffine ; the colours which they assume—violet, red, orange, gold-colour, and green—are due to superficial oxidation.*

German silver (Argentan, Pakfong, Maillechort) is an alloy of copper, nickel, zinc, or tin, which may be regarded as brass, with an addition of $\frac{1}{6}$ to $\frac{1}{3}$ of nickel. It has a yellowish white colour, a densely granular or jagged fracture, a spec. gr. of 8·4 to 8·7, and it is harder than common brass, but almost equally extensile. It takes a very high polish. In its preparation there are used zinc, copper, and nickel in a comminuted state. The metals are put in a crucible, a part of the copper being laid at the top and the rest at the bottom. The whole is then covered with charcoal powder and melted.

German silver takes a fine polish, and remains for a long time unchanged on exposure to the air ; it is less readily attacked by acid liquids than are copper and brass. The proportions of the ingredients are—copper 50 to 66 per cent., zinc 19 to 31, nickel 13 to 18·5. Latterly, smaller proportions of nickel are found in cheap sorts of German silver.

German silver can scarcely be distinguished on the touch-stone from a silver-alloy of 0·750. If the streak is moistened with nitric acid, it disappears more rapidly than that of silver, and on the addition of a solution of sodium chloride, no turbidity is produced. It is chiefly used in rolled sheets. Alfénide, used for candlesticks, milk-cans, tea services, forks, spoons, &c., is German silver electro-plated, containing about 2 per cent. of silver. Other plated nickel alloys are Peru silver, China silver, Christofle, and Alpacca. *Tiers Argent* consists of 27·5 silver, 62·5 copper, nickel, and zinc.

An alloy of nickel and silver has been used in Switzerland since 1850 for small coinage. It contains pieces for—

	Silver.	Copper.	Zinc.	Nickel.
20 raps . . .	15 ...	50	25 ...	10
10 „ . . .	10 ...	55 ...	25 ...	10
5 „ . . .	5 ...	60 ...	25 ...	10

A metal formerly met with under the name Suhler-white copper, contained 88 parts copper, 8·75 nickel, 1·75 antimony. It was obtained from old slag-heaps, and is the first nickel alloy which was used in the arts.

Copper Amalgam.—A compound of 30 parts copper and 20 mercury, obtained by moistening copper-powder with mercurous nitrate, covering with hot water, and adding the required amount of mercury by grinding. It is also known as metallic putty, and is a soft mass, which softens in a few hours. It is also (most injudiciously) used for stopping hollow teeth.

* Bessemer has effected great improvements in the preparation of bronze colours.—[EDITOR.]

LEAD.

Lead has been known from the remotest antiquity. It rarely occurs native, but frequently combined with sulphur, as galena (PbS), and as Bournonite, a lead and antimony sulphide. The latter ore consists of lead 41·77 parts, copper 12·76, antimony 26·01, and sulphur 19·46. It is worked for lead and copper. Lead is found also as cerussite, white lead ore ($PbCO_3$), pyromorphite, or green lead ore ($3Pb_3(PO_4)_2 + PbCl_2$), mimetesite, a lead arseniate ($3Pb_3(AsO_4)_2 + PbCl_2$), as Anglesite (lead sulphate, $PbSO_4$), yellow lead ore (lead molybdate, $PbMoO_4$), and as crocoisite, or red lead ore (a lead chromate, $PbCrO_4$).

Production.—Lead is obtained almost exclusively from galena. Its extraction depends on the behaviour of galena with metallic iron. If lead sulphide is heated with metallic iron, there are formed iron sulphide and metallic lead: $PbS + Fe = FeS + Pb$. The galena, previously freed from gangue by smelting or elutriation, is mixed with granular iron and smelted down in a shaft-furnace. The products are metallic lead and a lead matte. Instead of metallic iron, there may be used iron ores and slags, which exert a desulphurising action by means of their oxygen.

Figs. 172, 173, and 174 show a lead smelting furnace (sump-furnace). The hearth and the sump lie partly outside the furnace. The gases escaping from the shaft B, before reaching the chimney T, pass through chambers in which they deposit the particles of ore carried away by the blast *o*. The assorted ores mixed with granular iron are thrown into the furnace in alternate layers. The liquid products collect in the sump C. The products are slag floating on the surface, argentiferous lead and lead matte. The latter is either roasted and worked up for vitriol or cement copper or smelted with rich lead slags and granular iron, and worked for lead. The slag as it forms is allowed to flow off down an inclined plane until the sump is filled with the other products. The tap-hole is then opened, and the product run off into the lower hearth. In this hearth the matter as it congeals is taken off in discs; the subjacent work-lead is desilverised by the Pattinson process.

Fig. 172.

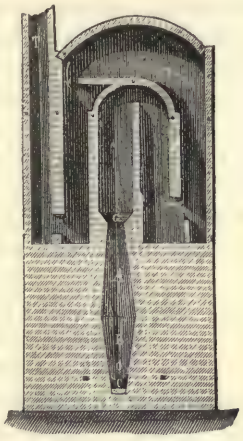


Fig. 173.

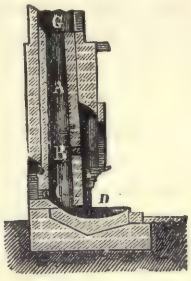


Fig. 174.



The production of lead from galena by roasting in the reverberatory depends on the behaviour of lead oxide and lead sulphate with galena. By the action of the oxygen of the air, a part of the galena is oxidised to lead oxide and sulphurous acid, whilst lead sulphate is also formed. By means of the oxygen of the lead sulphate and the lead oxide the sulphur of the undecomposed part of the galena is oxidised and removed:—$2PbO + PbS = 3Pb + SO_2$; $PbSO_4 + PbS = 2Pb + 2SO_2$.

If an excess of galena is present in the roasting process, there is formed lead sub-sulphide (Pb_2S), from which metallic lead is eliquated, whilst the residue takes up more sulphur: $Pb_2S = PbS + Pb$.

Upon this process, combined with the use of a reverberatory with a depressed hearth, is founded the English process for the production of lead. The ordinary arrangement of the reverberatories for melting lead ores in Derbyshire and Cumberland is shown in Fig. 175. The hearth, formed of slags fluxed together, rests on a

massive wall. Its surface is inclined from all sides towards the tap-hole, from which the lead flows down into the anterior crucible. The furnace has six doors *o*, three of which are at the tapping side, and three at the back. The ores are let down through a funnel T, capable of being closed down upon the hearth. In general 800 kilos. of ore are introduced and worked up in six to seven hours. The consumption of coal is about half the weight of the ore. The ore is spread level over the hearth, and the doors of the furnace are closed, that it may be heated uniformly. In two hours they are opened, until the smoke filling the furnace has disappeared, when they are closed and a strong heat is given. Subsequently the doors are opened for the second time and the ore is alternately stirred through one or other of the side doors. The mass becomes pasty, and the lead runs off on all sides. The stirring is kept up for an hour, and then the mass becomes almost liquid. This liquefaction is promoted by additions of fluor-spar. As soon as it is sufficiently fluid, the upper layer of the slag is run off and caused to solidify by wetting with water. It is called white slag; it has an appearance like enamel, and it often contains 22 per cent. lead sulphate. Coal is introduced through the middle door to congeal the refractory and abundant slag, which has remained upon the metal. Lastly the tap-hole is opened, and the lead runs off into the tap-crucible.

Fig. 175.

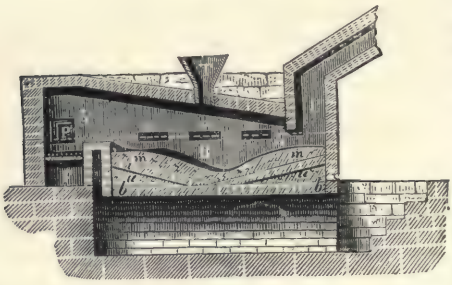
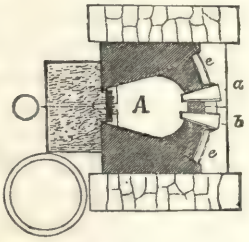
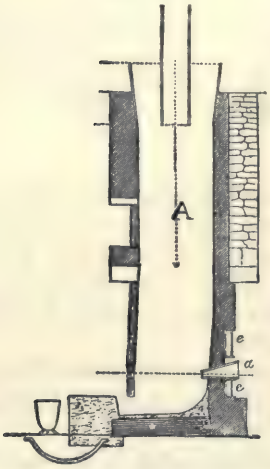


Fig. 176.



At Alternau the lead ore washings of the Upper Harz, containing 54–55 per cent. lead, 0·08 silver, 0·9 copper, 7–8 zinc, and 14–18 silica, are roasted in a reverberatory with one hearth. For smelting there are used two shaft-furnaces (Figs. 176, 177), the shaft of which, A, rises from the form 4 metres in a width of 1·2 metre, and then ends in a wrought-iron top-piece 1 metre in height, which expands above to 1½ metre. Up to 1 metre above the form the shaft has a gentle slope to form and rest, with which the front wall of *d*, the furnace, runs parallel. A wrought-iron water refrigerator, *e*, which forms a jacket for the back wall of the furnace, protects it against any corrosive action of the charge, without having too strong a cooling action upon the melting mass.

Fig. 177.



At present 4 tons of roasted ore are sorted with 1 ton of raw slick, and these 5 tons are charged, according to the proportion of silica and zinc, with 1 to 1·25 ton of puddling-slag, 1 to 1·25 ton of extraction residues from Oker, and 0·75 to 1·5 ton lime, in all 3·25 to 3·5 of basic materials. To this come slags from the same works as they may be needed. From such a charge there are obtained 32 to 34 tappings each, with 50 kilos. of coke, and 60 such lots are worked through in twenty-four hours, the pressure of the blast being 14 to 20 millimetres of mercury. The slag drawn off in the first quarter of 1882 contained—

Silica	30·32	Zinc oxide	7·27
Barium sulphate	0·19	Manganous oxide	1·66
Lead	1·13	Cobalt and Nickel	traces
Copper	0·18	Lime	16·15
Silver	0·0007	Potassa	0·67
Antimony	0·09	Soda	0·61
Ferrous oxide	35·72	Sulphur	1·47
Alumina	3·20	Phosphoric acid	2·04

If the proportion of metal in the slag is higher, it is a sign that more bases are needed for the decomposition of the lead silicate. If separation takes place in the sump of the furnace, and the slag falls below the normal amount, this indicates an excess of basic additions. The influence of the zinc present, which interferes with the course of the smelting, must be counteracted by decreasing the lime and increasing the iron in the charge, and by the addition of slags from the same work.

At Mechernich the ores are roasted in eighteen furnaces with double sides, with working-doors on both sides, and with rails laid on both the longer sides of the furnaces, for the sake of possible working on the sole of the upper hearth. Each furnace is 15 metres long by 4 in breadth, and the whole length available for roasting is 24 metres, with a width of 3·1 metres. There is room to receive 50,000 to 55,000 kilos. of ore, and the production of roasted ore is 8000 to 10,000 kilos. in twenty-four hours, so that a lot of ore remains from five to six days in the furnace, which is always kept full. The ore is kept constantly stirred up as it approaches the bridge. The imperfectly liquefied mass is let off every six hours in a form made of rails laid together in front of the furnace, and broken up when cold. There are used 15 per cent. of fuel for the vitreous product, which resembles obsidian, and has the following composition :—

Lead	58·85	corresponding to	PbS		3·47
			PbO		60·57
Copper	0·38	„	Cu_2S		0·48
Antimony	0·22	„	Sb_2S_3		0·30
Iron	2·70	„	Fe_2O_3		3·90
Zinc	0·82	„	Zno		1·05
Nickel	0·75	„	NiO		0·92
Manganese	0·36	„	Mn_2O_3		0·51
Alumina	4·80	„	Al_2O_3		4·80
Lime	0·31	„	CaO		0·31
Silica	23·65	„	SiO_2		23·65
Sulphur	0·66				

The fumes given off in roasting traverse a system of chambers of 10,015 cubic metres, and then a chimney 66 metres in height. The ore is melted in nine shaft-furnaces of 7 metres in height and 4·8 metres in length. The height of the furnace-shaft from the forms, which are placed in four bronze water-troughs, along the back wall to the mouth of the funnel of the working-door is 3·8 metres; the depth of the level of the forms 1·2 metre, with an enlargement to 1·5 metre at the top; the height of the crucible, moulded of sweepings, is 1 metre. For letting off the lead are two lateral tapping-channels opening into the crucible, 13 to 15 centimetres above its bottom; the tapping-hole for slags is 40 centimetres below the diameter of the forms. Iron pots suspended in trucks serve to receive the slag in such a manner that it flows over from a larger pot (interposed to keep back lumps of lead matte) into a smaller one. The charges for the furnace are placed in tilting-trucks, which (with the exception of the limestone) are raised by tackle to the level of the furnace-mouth. The charge consists of 100 parts of roasted ore, 5 parts of furnace bottoms, 35 iron-finery slags, 15 raw sparry iron, 45 limestone, 10 lead slags, and 25 coke. Of the nine shaft-ovens only four are in regular work, which get through 282,400 kilos. of charge in twenty-four hours, and yield 73,000 kilos. of work-lead. If the slag, which is daily

tested in an iron crucible with borax, soda, and a little tartar, yields more than 0·7 lead, it is re-smelted. The matte is ground, roasted, and mixed with the raw ores.

Matte.		Lead Slag.		Work-Lead.	
PbS	9·24	SiO_2	27·00	Silver	0·0215—0·0250
Cu_2S	1·95	P_2O_5	3·79	Copper	0·1332—0·1396
Sb_2S_3	0·40	Al_2O_3	5·61	Antimony	0·2180—0·1586
FeS	32·34	CaO	20·30	Iron	0·030 —0·014
NiS	0·40	Sulphur	1·26	Nickel	trace
SiO_2	0·31	Lead	1·02	Zinc	0·006
		Copper	0·35		
		Antimony	trace		
		Iron	25·81		
		Manganese	0·62		

Flue-dust.—According to Freudenberg, the deposit of flue-dust is proportional to the temperature of the gases and the size of the surface of the walls. Hence the deposit decreases more rapidly in the upper compartments of the chambers than in the lower. The proportions of silver, zinc, and antimony are greatest near the furnace, and decrease with the length of the flues. Samples taken contained 60·5 to 67 per cent. of lead, 3·2 to 4·2 zinc, 0·003 silver, 14·1 to 14·8 sulphuric acid, 5·4 to 6·2 sulphur, 1 to 2·1 ferric oxide and alumina, 5·8 to 8 coal, 0·3 to 0·4 antimony, 0·16 to 0·24 arsenic, and 0·6 to 4·1 lime. It appears, further, that the quantities of metals deposited in the smoke-channels as flue-dust are proportional to the square surface of the sides of the flues. He recommends, therefore, that metal sheets, &c., should be suspended parallel to the direction of the draught. Schlösser proposes the use of refrigerating pipes, and Walker that of electricity, which latter process is said to have proved unsuccessful.

Work-lead.—The work-lead obtained contains silver, copper, antimony, &c. For the separation of the silver, see SILVER. The litharge produced is either used as such or reduced to metallic lead. The reduction is effected in a reverberatory, the litharge being mixed on the hearth with charcoal. The lead thus obtained contains a little copper, antimony, and perhaps some silver. It is therefore less soft than lead produced from pure litharge. The composition of different sorts of Freiberg leads appears from the following analyses by Reich :—

	1.	2.	3.	4.	5.
Lead	97·72	99·28	87·60	90·76	87·60
Arsenic	1·36	0·16	7·90	1·28	0·40
Antimony	0·72	trace	2·80	7·31	11·60
Iron	0·07	0·05	trace	0·13	trace
Copper	0·25	0·25	0·40	0·35	trace
Silver	0·49	0·53			

Electric Production of Lead.—The process of Blas and Miest is based on the fact that the native sulphides conduct electricity when they are compressed into plates, with the aid of heat. To this end zinc blende, galena, &c., are comminuted to grains of about 5 millimetres in diameter, pressed into plates in metal moulds, under a pressure of 100 atmospheres, heated to 600° in a furnace, pressed again and quickly cooled, that they may be easily extracted from the moulds. Plates of galena thus obtained are suspended as anodes in a bath of lead nitrate. There is here little chemical work to be performed, as, according to $Pb(NO_3)_2 + PbS = Pb(NO_3)_2 + Pb + S$, the work needed at the negative pole for the decomposition of the lead nitrate is compensated at the positive pole, so that chemical work is needed only for decomposing the lead sulphide; hence, for 1 kilo. lead 18·328 : 207 = 89 heat-units. If we take into account resistance, transportation

of ions, &c., or only a 30 per cent. utilisation of the power of the machine, we should have hourly for each horse-power 2 kilos. of lead and an equivalent quantity of sulphur. Practically speaking, the matter is still involved in difficulties.

Keith's process for refining lead by electrolysis is carried out by the Electrometal Refining Company of New York. In each of a set of 30 vats, 1 metre in height and 1·83 metre wide, there are immersed as kathodes 13 cylinders of thin sheet brass, arranged concentrically, so that they are 0·61 to 1·83 metre in diameter. They are immersed to a depth of 0·6 metre. The crude lead, smelted in a reverberatory, is poured into 12 moulds 61 centimetres long, 15 broad, and 3 millimetres in thickness, to form plates for the anodes. The solution of lead sulphate (nitrate?) and sodium acetate is forced from below continuously into the vats, through wooden pipes laid below the vats, whilst it flows off above to be heated in a cistern to 38° by means of steam pipes, and again conveyed to the vats, so that it is in constant circulation. The muslin bags enclosing the anodes retain silver, along with arsenic, antimony, &c. The silver is melted along with saltpetre and soda. The lead, before and after this treatment, has the following composition :—

	Crude.		Refined.
Lead	96·36	...	99·9
Silver	0·554	...	0·00007
Copper	0·315	...	0
Antimony	1·070	...	trace
Arsenic	1·22	...	trace
Zinc and Iron . . .	0·489	...	0

If 12 h.-p. are used, 10 tons of lead are refined in 24 hours, in 48 vats, each containing 50 plates weighing each 16 kilos. Consequently, if 1 h.-p. requires 1·75 kilos. of coal hourly, 67·1 kilos. of coal are used per ton of lead.

Properties.—Lead as it occurs in commerce, refined and Pattinsonised, has a peculiar light grey colour. It is little disposed to assume a crystalline texture, and has on its fracture a uniformly melted appearance. In certain metallurgical processes it may be obtained crystallised in the forms of the tesseral system (combination of cubes and octahedra). Lead is distinguished by softness and flexibility; hence, it has a somewhat high degree of malleability, but little absolute tenacity. If freshly scraped or cut, it is very brilliant, but it soon becomes dull on exposure to the air. It marks strongly on the hands, on paper, and on linen fabrics. The spec. gr. of refined lead is 11·370; that of cast lead, 11·352, and that of rolled lead, 11·358. In the manufacture of sheet lead oxidation has to be avoided. Lead is one of the easily fusible metals; it solidifies quietly, *i.e.*, without spirting, and with a concave surface. If heated almost to the melting-point it becomes brittle, and breaks under the hammer in fragments of a peculiar rod-like structure. If heated to a certain degree, it may be pressed into solid or hollow cylinders: the former serve for projectiles and the latter for pipes, which are now manufactured on a large scale. At a full white heat, and if air is excluded, it enters into ebullition and evaporates. Lead takes up at most 1·5 per cent. of zinc and 0·07 per cent. of iron, but so much the more copper as the temperature rises.

The uses of lead are very various. It is employed in the form of rolled plates for roofing, for boiling-pans for sulphuric acid, copperas, and alum; lead chambers in the manufacture of sulphuric acid; water- and gas-pipes and retorts; in thin leaves for wrapping up snuff; in the manufacture of small shot and bullets; in metallurgical processes for the extraction of certain metals, *e.g.*, silver and gold; for the production of sugar of lead, red lead, white lead, and other lead preparations.

Manufacture of Small Shot.—Shot is remarkable as no moulds are needed in its preparation. It consists of solidified drops of lead. The lead is not used pure, but alloyed with a small quantity of arsenic, 0·3 to 0·8 per cent., which gives it the power of granulating more easily. Too much arsenic gives the grains a flattened aspect, and

too small a proportion renders them longish. The arsenic is added either as such, as sulphide, or as arsenious acid. If it is used in the last state, the surface of the lead is covered with charcoal powder, the heat raised to redness; the arsenic, wrapped in coarse paper, is placed in a basket of iron wire, plunged into the melted lead, and well stirred. For granulating the lead there are used iron kettles, with a flat bottom, provided, like a sieve, with round holes of equal diameter. If the lead were at once poured into the kettles, there would be produced more oval than round grains. There is therefore placed in the kettle a porous mass, which attaches itself to the sides, and keeps the lead at such a temperature that it flows through, neither too easily nor too tardily. The substance used is the dross drawn off from the surface of the molten metal. As the liquid metal oozes through this mass, and flows in single drops through the holes in the kettle, it takes a globular form in falling, like every other liquid. The grains, congealed whilst falling from a great height, are received in water which holds in solution in 100 parts 0·025 sodium sulphide. A thin film of lead sulphide is thus formed round the grains, and defends them from oxidation.

Alloys.—Soft solder, for tinmen, &c., consists of equal parts lead and tin; organ-pipe metal (96 parts of lead and 4 of tin); antifriction metal (4 tin, 5½ lead, and 1 antimony); hard lead (an alloy of lead and antimony); the alloy for ships' nails (3 parts tin, 2 lead, 1 antimony); the calain of the Chinese, used in foil for lining tea-chests (126 parts lead, 17·5 tin, 1·25 copper, and a trace of zinc). Other alloys, such as type-metal, are mentioned under ANTIMONY.

Production of Lead.—The annual production of lead for the whole of Europe was, in 1885, 330,000 to 350,000 tons, and that of North America 120,000 tons. The annual average consumption of lead may be estimated as:—North America, 135,000 tons; Britain, 115,000; France, 6500; Germany, 45,000; and the rest of the world, 100,000 tons: in all, 460,000 tons. The consumption in France for lead pipes and lead plates has decreased to a very remarkable degree.

SILVER.

Silver occurs in nature very abundantly; partly metallic (usually auriferous); partly combined with arsenic, antimony, tellurium, and mercury; partly as sulphide, mingled with other sulphides; and partly as a chloride. The most abundant silver ores are:—Argyrose (silver glance), Ag_2S; argyrythrose (dark-red silver), Ag_3SbS_3; proustite (light-red silver), Ag_3AsS_3; miargyrite, $Ag_2Sb_2S_4$, with small proportions of copper and iron; psaturose (prismatic melane glance, brittle silver sulphide), $CuAg_2S + Sb_2S_3$; polybasite, $[(Ag_2SCu_2S)9Sb_2S_3]$; and freieslebenite $[(FeS,ZnSCu_2S)_4, Sb_2S_3 + (PbSAg_2S)_4Sb_2S_3]$.

As chloride (horn silver), $AgCl_2$, silver occurs in some quantity in Utah.*

Lastly, silver occurs in galena, which contains 0·01 to 0·03, sometimes 0·5, rarely 1 per cent.; in copper ores, copper pyrites, chalkosine, and phillipsine, with 0·020 to 1·1 per cent. of silver; in cupriferous pyrites (from which, when burnt, silver and copper are now obtained); in the fahl ores, in blende, and calamine.

Extraction.—Silver is obtained—

I. In the wet way.
 1. By means of mercury amalgamation.
 2. By solution and precipitation, on the systems of Augustin, Ziervogel, and other procedures.

II. In the dry way.
 1. Obtaining argentiferous lead.
 2. Extraction of silver from argentiferous lead.

* Silver chloride exists in solution in sea water, but the quantity is so small that its extraction is not remunerative.

Silver is rarely smelted out from its ores, which can be undertaken only with such as are rich in native silver. The silver thus obtained is mostly rich in gold, and is submitted to the process of refining.

Amalgamation.—The extraction of silver by means of mercury, or the amalgamation process, is followed in the case of very poor silver ores (argentiferous copper matte, speiss, &c.).

In the process as formerly used in Europe, 10 per cent. of common salt was added to the ores to be amalgamated, and the mixture was roasted to drive off antimony and arsenic. By the mutual action of the salt and the roasted pyrites, were formed sodium sulphide, ferric chloride, and escaping sulphurous acid; further copper sulphate, and ferric sulphate, which oxidised the untransformed part of the silver sulphide to silver sulphate, being themselves reduced to cuprous and ferrous sulphates. By the action of the residual salt were formed silver chloride and sodium sulphate. The other metals present were, like the silver, converted into chlorides. When the roasting was completed the brown mass was ground and placed in the amalgamation vats, in which they were mixed with water, scrap iron, and mercury, and turned for 16 to 18 hours. The metals were precipitated on the iron and became amalgamated with the mercury.

To explain the nature of the amalgamation process, let us suppose that a silver ore: Cu_2S, Ag_2S, $FeS + As_2S_3$, Sb_2S_3, is being worked. After the roasting with salt there are found Cu_2Cl_2, $2AgCl$, $FeCl_2$, $3Na_2SO_4$, and As_2O_3, Sb_2O_3, $6SO_2$.

For the amalgamation vats there are produced by the joint action of the iron, mercury, and water:

$$Cu_2Cl_2, 2AgCl, FeCl_2 + Na_2SO_4 + 2Fe + nHg = Na_2SO_4 + (Cu_2, Ag_2, nHg) + 3FeCl_2.$$

The amalgam collects at the bottom of the vats, and is let off by means of a spigot turning downwards, through straining cloths of ticking, into stone troughs.

In order to separate the superfluous mercury, the sack is tied at its mouth and pressed between boards. The solid amalgam remaining in the bag, and containing about 11 per cent. of silver and 3 to 4 per cent. of copper, is laid on iron plates in the apparatus for distilling mercury (*q.v.*). The cupriferous silver (plate silver) is left behind.

The American, or wet amalgamation (patio process) is practised in Mexico, Peru, Chile, Bolivia, and in the Western States of North America. The silver ores are stamped whilst dry, and then finely ground with water. The stamped ore is conveyed to the ore-mills (Arrastras) and ground with the addition of water. The thin mud is conveyed to a court (patio) laid with stone flags slightly sloping, so that the rain-water may run off. The ore-mud, to which from 2 to 5 per cent. of common salt is added, is well trodden by mules or horses. After a few days there is added *magistral*, roasted copper pyrites, therefore essentially copper sulphate. This is also well trodden in, and by degrees mercury is added, about six times the weight of the silver contained in the ore (Incorporation). The treading is continued on alternate days for a term of two to five months, until the mass seems completely de-silvered. The mud is then washed in cisterns of masonry to separate the amalgam, which is freed from superfluous mercury by pressing in bags of ticking, and distilled at a reduced pressure.

In the amalgamation process as generally followed in America, copper chloride and silver, according to Rammelsberg, form cuprous chloride and silver chloride—

$$2CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2.$$

Silver sulphide is completely decomposed at a boiling heat by copper chloride—

$$Ag_2S + CuCl_2 = 2AgCl + CuS.$$

Sodium chloride has a solvent action upon silver chloride and accelerates the process of decomposition. Cuprous chloride and silver sulphide yield silver chloride and dicuprous

sulphide: $Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S$. If cuprous chloride is previously dissolved in sodium chloride the transformation is more rapid, but a quantity of silver chloride remains in the liquid. If zinc is added to the separated mixture and the solution of common salt is heated, there remains a mixture of 2 molecules silver and 1 molecule Cu_2S. Copper chloride and arsenic sulphide yield quickly copper sulphide and arsenious chloride: $As_2S_3 + 3CuCl_2 = 3CuS + 2AsCl_3$. On the other hand, the greenish grey deposit obtained by the action of copper chloride upon antimony sulphide, Sb_2S_3, contains, along with sulphur and copper, much antimony, as also chlorine and oxygen, in consequence of the decomposition of antimony chloride by water and formation of oxychloride. But a great part of the antimony remains in the solution, which contains sulphuric acid. As the analysis shows that the separated copper and chlorine exist in the same proportions as in cuprous chloride, we may assume that the rest of the chlorine has oxidised a part of the sulphur. Cuprous chloride and antimony sulphide behave in a similar manner, but the copper seems to be present chiefly in the metallic state in the matter deposited, which also contains antimony oxychloride and, on standing, antimonic acid is deposited from the richly cupriferous filtrate. Both kinds of red silver ore (argyrythrose and proustite) are decomposed by cupric chloride. In the separated mass, which is black in the arsenical ore and grey in the antimonial, there are found the silver, the antimony, but only half the arsenic. The silver is entirely found as chloride in argyrythrose, but only to the extent of one half as proustite; the rest of the deposit consists of copper sulphide and free sulphur.

Among the usual modifications of the amalgamation process, one treats the ore with water, salt, and mercury, in presence of iron or copper; the other employs water, salt, copper chloride, and mercury. The first method figures in the tina process, using a wooden vat with an iron bottom, and, in the cazo-oder calderon process worked, with the addition of salt, in wooden or stone vessels, and the washoe process, which requires iron kettles and runners. The two latter methods require the aid of heat.

The second method comes into play in the patio process, above described; and characterised by the use of magistral. The choice of the two principal processes depends on the chemical character of the ores. The first requires that the main mass of the silver should be native, as is the case in the pacos in Peru, in the metas calidos in Chile, and the Colorados in Mexico, which often contains silver chloride and bromide. The silver is easily amalgamated, as are also the chloride and bromide if copper or iron is present. The sulphur compounds existing at greater depths—silver glance, argentiferous fahl-ores, and pyrites—must be treated by the patio process. Though Rammelsberg's experiments prove that silver sulphide and argyrythrose can, under favourable circumstances, be reduced by copper chloride, it is still very doubtful whether this process can extract the whole of the silver from sulphur ores on the large scale.

The Kröncke process, which has been in use in Northern Chile for some time, consists in amalgamation, in vats, in which the agents are cuprous chloride, zinc, and mercury. The air is almost excluded, and the amalgamation is effected within a few hours. Experiments have shown that the sulphur ores can thus be completely decomposed, and the results of the process are described as very satisfactory.

Extraction of Silver by Solution and Precipitation.—The ores are here roasted, either alone or after the addition of salt. For the latter method the roasting furnace of Stetefeld has proved successful. The ore, mixed with from 2·5 to 18 per cent. of sodium chloride, slides down in the shaft *B* (Fig. 178), from 9 to 14 metres in height, meeting at *O* the hot gases coming from the fires at *G*, whilst air enters at *M*. The doors, *P* and *R*, serve for watching and regulating the process. The roasted ore is let fall into the recipients, *N*, by opening a trap, *C*, at the bottom, and is here slowly cooled to complete the chlorination. The gases escape through the shaft *H*, provided with

man-holes, *S*, and additional fire, *E*, in order to deposit their flue-dust in the funnels, *F*. With large furnaces and great quantities of ore operated upon, 50 per cent. of the ore collects in the flue-dust chambers, of which 80 per cent. settles in the first compartment. In order to effect the chlorination of any silver that has escaped the action of chloride in the furnace, the flue-dust chambers are only emptied occasionally, the last compartment once weekly. The escaping gases enter a chimney not less than 16 metres in height. In the same furnace the weight of ore worked in 24 hours is

Fig. 178.

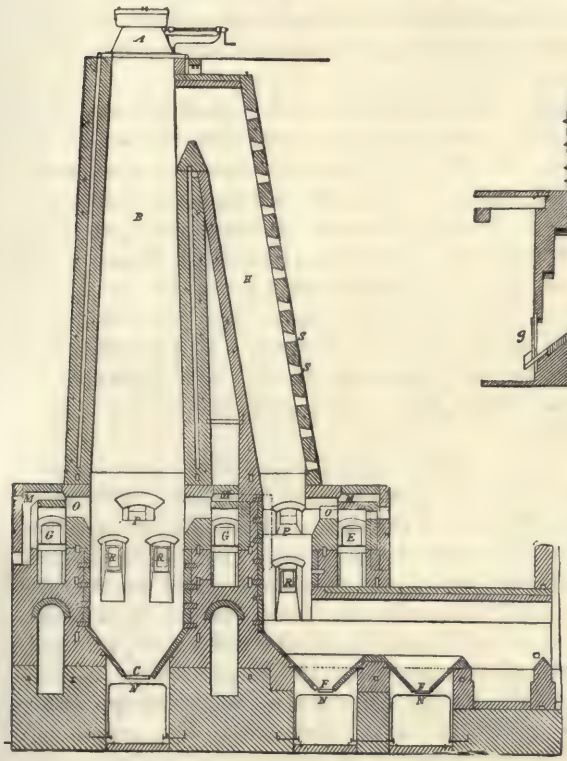
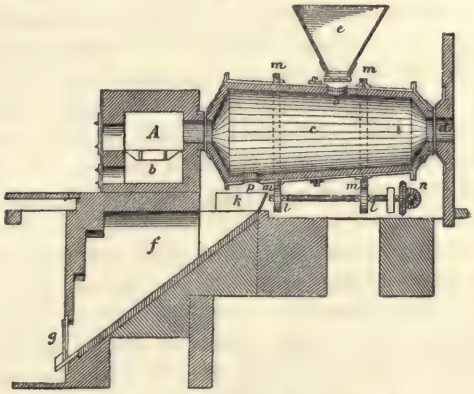


Fig. 179.



70 tons of ores poor in sulphur, but only 30 tons of ores of such as contain pyrites and blende. As the roasting is very rapid the loss of silver here is said to be smaller than in a reverberatory. The coarseness or fineness of the ore is regulated by the manner in which it is to be afterwards treated. If the ore is intended for amalgamation it must be ground more finely than if it is to be submitted to lixiviation (with sodium thiosulphate) as mercury cannot be entirely washed out from coarsely ground ores. The rotatory furnace of Brückner is used in many places. The modification proposed by Arent (Fig. 179) has the object that in the part of the cylinder, *c*, situated nearest to the fire, *A*, the ore is more heaped up than towards *d*. The revolving furnace is filled through the hopper, *e*, and the aperture, *o*, and emptied through *p* into the iron chest, *k*, or the recipient, *f*, provided with a sliding door, *g*. The rotation is effected by the rollers, *l*, and the cast-iron rings, *m*.

Augustin's Process.—The most ancient hydro-metallurgical process for extracting silver is that of Augustin—the so-called salt lixiviation. It depends on the formation of an easily soluble double chloride when silver chloride is brought in contact with an excess of strong solution of common salt with the aid of heat, and on the power of copper to expel the silver completely from the saturated solution of this compound. The copper-matte, consisting chiefly of silver, copper, and iron sulphides, are reduced to fine powder by stamping and grinding, and are roasted at first without salt. There is then formed, first iron sulphate, then copper sulphate, and lastly, as the temperature is raised, silver sulphate, by which time all the iron sulphate and a great part of the copper sulphate are decomposed, so that the mixture at the end of this preliminary

roasting consists of iron oxide, copper oxide, and small quantities of copper sulphate. By continuous roasting with common salt the silver sulphate is converted into silver chloride. The mass is then lixiviated with a hot saturated solution of salt, which dissolves the silver chloride. From the liquid the silver is precipitated by metallic copper, and the copper is recovered from the coppery solution by means of metallic iron.

(For the extraction of silver from burnt pyrites see SULPHURIC ACID.)

Ziervogel's Process.—In this lixiviation process no salt is added on roasting. The roast ore, consisting mainly of silver sulphate, a little copper sulphate, much copper oxide and iron oxide is extracted with hot water, which dissolves the silver and copper sulphates. From this solution silver is precipitated by metallic copper, and copper sulphate is obtained as a by-product.

At Mansfeld this process has been in use for many years for desilverising copper matte. The lixiviation is rapidly effected ; whence there is a less outlay for fuel and for labour than in the Augustin process. On the other hand, the roasting is less easily effected, richer materials are needed, and, as a rule, the residues are richer. In presence of arsenic and antimony the Ziervogel process is inapplicable, since on roasting there are formed silver arseniate and antimoniate, insoluble in water. The presence of lead easily leads to fritting, which makes the roasting difficult.

Other Procedures.—Of late ores of gold and silver have been extracted with sodium thiosulphate (formerly known as hyposulphite of soda). This process is in use in California and Nevada, after the ores have been roasted with 3 per cent. of common salt : $AgCl + Na_2S_2O_3 = NaCl + NaAgS_2O_3$. The solution is mixed with a solution of calcium sulphide :

$$2NaAgS_2O_3 + 2NaCl + CaS = Ag_2S + 2Na_2S_2O_3 + CaCl_2.$$

The lye drawn off from the precipitated silver sulphide is used again. Care must be taken that no excess of calcium sulphide is present, as this would subsequently occasion a precipitation of the dissolved silver in the lye-vats in the state of silver sulphide. Such silver would not be redissolved in the thiosulphate, and would consequently be lost. If the ore contains gold it is preferable to use calcium thiosulphate. This salt is prepared by boiling lime with sulphur, $3CaO + 12S = 2CaS_5 + CaS_2O_3$, letting the solution subside, and passing sulphurous acid into the clear lye till the sulphide is converted into thiosulphate and a dilute solution of silver is no longer precipitated.

According to Russel, ores which contain silver in combination with arsenic and antimony, and from which the precious metals cannot be extracted by lixiviation with sodium thiosulphate, can be treated either at once or after mixing with thiosulphate, with a solution produced by mixing thiosulphate with a solution of copper, preferably copper sulphate. There is formed according to the equation :

$$4Na_2S_2O_3 + 2CuSO_4 = 2CuS_2O_3.Na_2S_2O_3 + 2Na_2SO_4 + Na_2S_2O_3,$$

a sodium copper thiosulphate, in which silver is easily substituted for copper.

Extraction of Silver in the Dry Way.—The extraction of silver from its ores by means of lead depends—(*a*) On the property of lead to act upon silver sulphide with formation of lead sulphide and separation of metallic silver. Other sulphides accompanying the silver, especially copper and iron sulphides, are less readily decomposed by lead. The products of the fusion are argentiferous lead and a matte free from silver, but containing lead, copper, and iron sulphides. The extraction of silver by lead is the more complete the poorer are the ores in copper.

(*b*) On the decomposing action of lead oxide or lead sulphate upon silver sulphide :

$$Ag_2S + 2PbO = Pb_2Ag_2 + SO_2.$$

(*c*) On the reducing action of lead upon silver oxide or silver sulphate :

$$3Pb + Ag_2SO_4 = PbAg_2 + 2PbO + SO_2.$$

(*d*) On the greater affinity of silver for lead than for copper. If argentiferous

copper is melted up with lead there is formed an easily fusible argentiferous lead and an alloy of copper and lead which melts with difficulty. The former can be separated from the latter by eliquation.

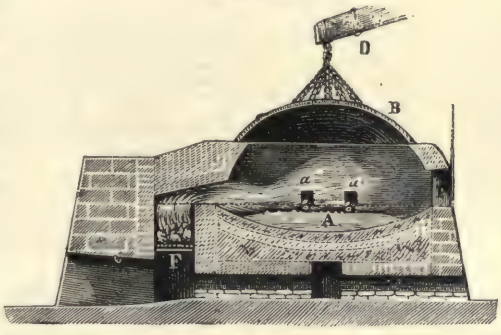
To this process there are subjected genuine silver ores, roasted pyritic ores, argentiferous copper and lead ores raw or roasted, and roasted argentiferous native arsenic. The essential feature of the process is the treatment of the materials with melted lead. An argentiferous work-lead is formed just as in the treatment of galenas containing silver.

The treatment of the work-lead may be effected (1) on the refiner's hearth, (2) by the Pattinson process, and (3) by the Parkes process (by means of zinc).

The refining on the hearth turns on the fact that the readily oxidisable lead is separated by a simple oxidising fusion from the non-oxidisable metals, care being taken that the lead oxide formed is partly drawn off and partly absorbed into the pores of the hearth. The surface of the metallic bath is oxidised as long as the alloy contains lead, and the silver remains behind.

The hearth is a round reverberatory, with a fire-box F built up to it (Fig. 180). The hearth A is covered with a hood *a*, of sheet-iron, lined with fire-clay B which can be raised or lowered by the arrangement D. The hearth is made of lixiviated ashes, or preferably of calcareous marl; in the middle is a depression to collect the silver. In the space surrounding the hearth is the litharge-hole, during working kept closed with the same material of which the hearth is made so far that it is on the same level as the upper surface of the melted lead in the furnace, so that the litharge formed upon the metal may flow off. As soon as the quantity of the work-lead decreases the mass in the litharge-hole is partially removed; this channel-like depression is called the litharge road. The hole P opposite the fire-bridge serves for introducing the hearth-mass and the materials. The tuyères of the blast open at *a*.

Fig. 180.



The refining is continued until the silver on the hearth is covered only with a thin film of litharge, which disappears as rapidly as it is formed. The formation and disappearance of the film is recognised by a play of colour—the *brightening* of the silver.

As soon as this phenomenon is recognised the firing is ceased, the silver is cooled by sprinkling with water, and lifted out of the furnace. The liquid lead-oxide flowing off congeals on cooling to a foliaceous crystalline mass of a yellow or reddish-yellow colour, litharge.

The Pattinson Process.—The rule holds good that work-lead with a percentage of silver less than 0·12 cannot be further refined by cupellation. The process indicated by Pattinson (in 1883) is based on the phenomenon that if we melt a sufficient quantity of lead in an iron kettle and let the liquid mass cool uniformly there are formed small octahedral crystals which cohere at their ends. These crystals are much poorer in silver than the original alloy, whilst the silver is concentrated in the part which remains liquid. If we melt these crystals and proceed as before, there are again formed crystals, which are still poorer than the foregoing. By a succession of such separations the lead is resolved into two portions, a small part rich in silver, rich lead (containing 0·5 to 1·5 per cent. of silver), and a larger portion, very poor lead (containing 0·001 to 0·003 per cent. of silver). As the limit up to which the lead can be enriched by the Pattinson process, we may fix 2·5 per cent. of silver.

A desilvering of lead by means of zinc was proposed by Parkes in 1850.

Work-lead is placed in an iron pan; when melted 5 per cent. of melted zinc is added, and after thorough stirring the mixture is let stand until the zinc congeals to a cake, which is lifted off. The zinc in the earlier process was separated from the silver by distillation. After the completion of the distillation the residue is taken out, mixed with some lead, and refined on the hearth. According to a modification, introduced by Cordurié, the zinc is oxidised by superheated steam ($Zn + H_2O = ZnO + H_2$). The zinkiferous work-lead left after being thus desilverised is freed from zinc by heating with lead chloride, as a mixture of lead sulphate and sodium chloride, then lead chloride is formed ($Zn + PbCl_2 = ZnCl_2 + Pb$). According to Flach's proposal the zinkiferous lead is treated with puddling slags in a shaft-furnace to scorify and volatilise the zinc. The zinc process has become almost universal in Britain, France, and Germany.

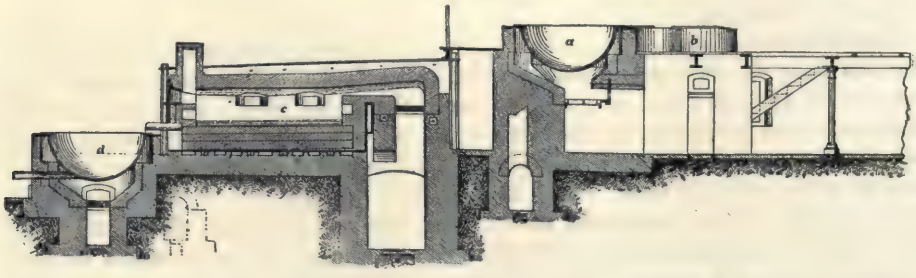
The advantages to which this process is indebted for its rapid introduction consist, according to Plattner, especially in the circumstances that—

1. The process does not require the work-lead to be previously refined, so far as the removal of inconsiderable quantities of copper, arsenic, and antimony is concerned;
2. The work is effected with only small quantities of intermediate products;
3. That it requires a smaller apparatus with fewer workmen and a reduced outlay for fuel;
4. That it effects the separation of silver from lead in much shorter time than the Pattinson process;
5. That it yields a decidedly smaller and proportionally richer quantity of rich lead to be refined; and lastly,
6. That the process involves a more moderate loss of lead.

A further advantage of the Parkes process is that a minimum proportion of gold, present in the work-lead, can be first extracted by a small addition of zinc, and a zinc scum obtained which furnishes a small quantity of auriferous silver, whilst the subsequent main quantity of silver extracted by a second treatment with zinc is free from gold.

At the Mulden Works at Freiberg the Pattinson and Parkes processes are combined in such a manner that the former process is interrupted in that pan where it is expected that bismuth may be obtained, which passes into the rich lead. In the Pattinson process there is here employed a battery of 9 cast-iron pans, each of 1·75 metre diameter at top, 0·90 metre in depth, and receiving each a charge of 150 hectokilos. For the Parkes process (Figs. 181–184) there are set up, with separate fires: 2 cast-

Fig. 181.

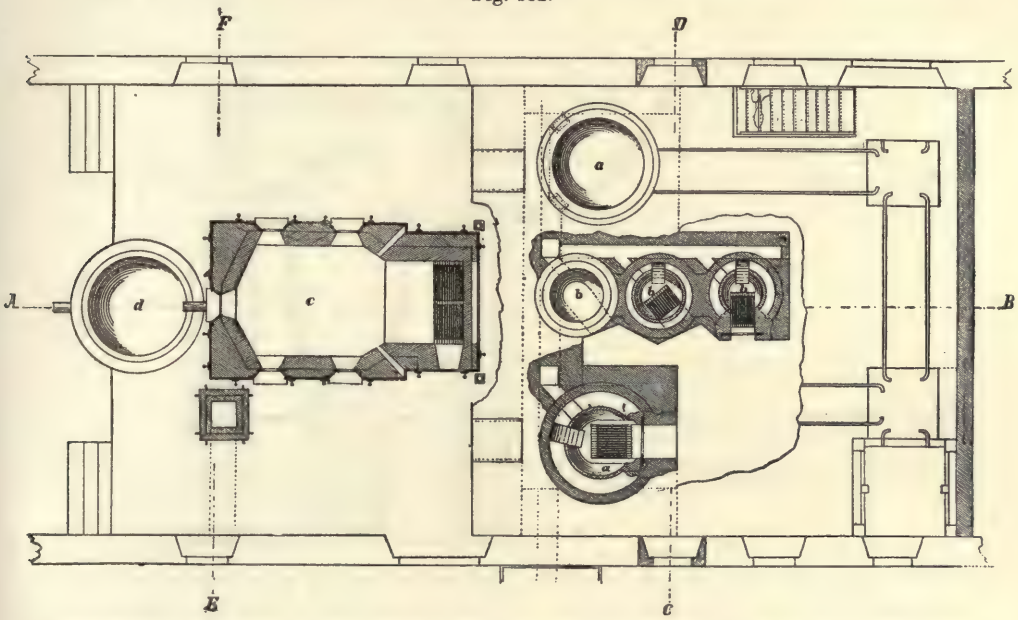


iron desilvering pans, *a*, of 1·98 metre top-diameter, 1·0 metre in depth, and each holding 200 hectokilos.; 3 cast-iron hemispherical eliquation pans, *b*, of 0·55 metre; 1 refining furnace, *c* with a fire-clay hearth 3 metres long, 2 metres wide and 0·45 metre

deep for freeing the poor lead from zinc, and 1 cast-iron pan, *d* of 1·9 metre diameter at top and 1 metre deep to receive the poor lead when freed from zinc.

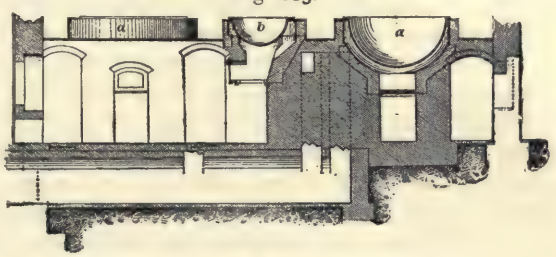
The apparatus for the Parkes process is so united with the Pattinson apparatus that the two desilvering pans and the three eliquation pans of the Parkes process, placed at the same level, lie with their edge 2 metres higher than the edge of the Pattinson pans,

Fig. 182.



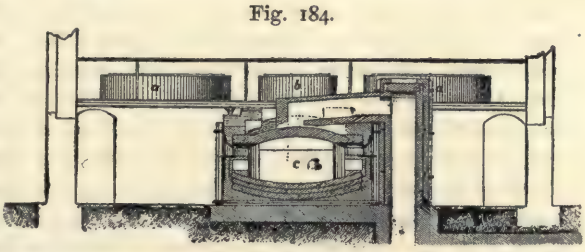
so that the zinkiferous poor lead can be conveyed by means of syphons (Fig. 185) whilst still liquid, into the following refining-furnace placed with its sole 2 metres lower than the margin of the desilvering pans. The pan for the de-zinkified poor lead is built in with its margin 10 centimetres below the sole of the refining furnace.

Fig. 183.



From it the poor lead can be led off through pipes (which can be closed by a conical valve) and a movable channel. It is then run into cast iron moulds to give it a form suitable for trade. The conveyance of the lead from the Pattinson battery and of other refined work-leads, poor in silver, to the level of the desilvering pans is effected by a simple steam lift. The last pan of the Pattinson battery is emptied of the work-lead containing 0·1 per cent. of silver and destined for the Parkes process by means of the Rösing steam-pump. For mixing in the zinc there is used an agitating scoop, 2·3 metres in length with 100 to 120 holes to let the lead drop through (Fig. 186); for lifting off the zinc scum there is used a similar scoop with a shorter handle. For distilling

Fig. 184.



the rich scum there are used two wind-furnaces (Fig. 187) with a round shaft 0·75 metre in width and 0·9 metre deep down to the level of the grate. On the movable ring *e*, of angle iron and strong sheet iron lined with fire-clay lies a cover, *f*, of clay plates resting in a ring of angle iron. The ring and the cover can be lifted off either separately or jointly by means of pulleys.

The graphite crucible is 55 centimetres high, with sides 5 centimetres thick; the

Fig 185.



Fig. 186.

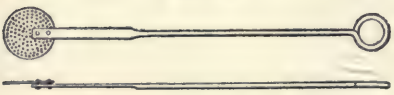
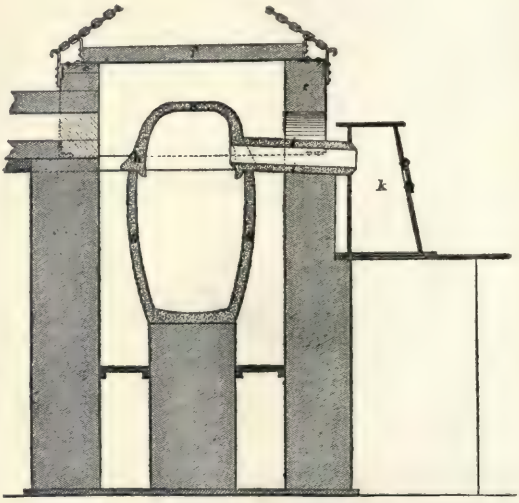


Fig. 187.



cover, of graphite, *h*, 20 centimetres; the graphite pipe, *i*, is 50 centimetres in length, with sides 2·5 centimetres in thickness. The iron receiver *k*, ½ metre in height rests on an iron bottom plate and has a movable lid. All the refined work-leads containing more than 0·1 per cent of silver, if not worth separate treatment on the hearth, are conveyed to a pan of the Pattinson battery, according to their proportion of silver, and are there worked to a rich lead of 2 per cent. and a poor lead of 0·1 per cent. The rich lead goes to the refinery hearth and the poor lead to the Parkes process.

To desilver this work-lead by means of zinc, after the lead has been fused in the desilvering-pan, the solid pieces formed are lifted off with the scum scoop, until the lead-bath has a perfectly clean surface. When the lead has been heated up to the melting point of zinc (by means of a cover), the first addition of zinc takes place. When it has been thoroughly stirred into the lead, the mixture of metals is left undisturbed until a crust, about 3–4 centimetres in breadth, has been formed at the edge of the pan. The zinc scum, which has come to the surface and covered it, must be lifted off with the perforated scoop, letting the adhering lead carefully drop back. The zinc scum from the first additions of zinc being rich in silver (rich scum) is transferred to the adjacent eliquation pans, whilst the scum poorer in silver (poor scum), obtained from the subsequent additions of zinc, is thrown into iron pans, and is afterwards used in desilvering a fresh charge of work-lead, so as to utilise its zinc. At the same time that the scum is removed, the fire under the pan is strengthened, in order to give the lead the high temperature required for the next addition of zinc. The entire treatment is repeated as often as additions of zinc are necessary, in order to extract the silver from the work-lead, and convert it into poor lead.

After the (supposed) last skimming, the sides of the pan are carefully scraped with a chisel, in order to remove any adhering scum and bring it to the surface, lest the accuracy of the determination of silver in the poor lead should be endangered. An intensified fire promotes the fusion of the scum. Before each fresh addition of lead the

metallic bath is well stirred up, and several samples of lead are taken from the middle with a sampling-spoon, cast into ingots, and tested for their contents of silver. If the assay gives a result of 0·001 per cent. no more zinc is added, and the process is regarded as complete. As soon as the zinkiferous poor lead has been rendered sufficiently hot, it is drawn off from the pan (by means of the syphon, previously heated and filled with melted lead) into the sheet-iron gutter, leading to the hearth of the refining furnace, and the desilvering pan when empty is filled again for a new operation.

Simultaneously with the desilvering, goes on the eliquation of the rich scum in the first, and afterwards in the second, eliquation pan. The argentiferous zinkiferous lead obtained by this process goes back, like the poor lead, to the desilvering process, whilst the rich silver scum, which has been taken off, is reserved for distillation. The average time needed for melting the work-lead and taking off the cakes is five hours, and for each period of the desilvering, *i.e.*, from one addition of zinc to the next, is altogether five hours, namely :

	hr.	min.
Heating the lead-bath	1	15
Adding and melting zinc	0	45
Stirring in zinc	0	30
Cooling metallic bath	2	0
Lifting off zinc scum	0	30

As for the work-lead from the Pattinson process containing 0·1 per cent. of silver at the most three additions of lead are sufficient ; the duration of the desilvering of such work-lead, the time required until a zinkiferous poor lead is produced, may be taken at the most as twenty hours.

Every charge of 200 hectokilos. (20 tons) of work-lead of the above-mentioned percentage of silver, with the additional use of the zinkiferous eliquation lead and the poor scum, requires for desilvering, 215 kilos. of zinc, 100 kilos. for the first addition, 75 for the second, and 40 for the third. The addition of zinc required for desilvering runs up to 1·485 per cent., whilst the actual consumption of zinc, deducting that recovered on the distillation of the rich scum, is only 0·832 per cent., the original proportion of silver 0·1 per cent., and the gold averaging 0·0004 per cent. of the work-lead, is reduced after the first addition of zinc to 0·0250 silver and a trace of gold ; after the second to 0·0020 silver, and after the third to 0·0007 per cent. silver, and no gold. As a rule, the decrease of the proportion of silver is most striking after the first addition of zinc, whilst the last small quantities of silver are more difficult to remove. The process is essentially abbreviated if the first addition of zinc is made as large as practicable. The cost of the zinc is not increased, as there is effected an economy in the subsequent additions of zinc, as well as in time. The gold generally disappears after the first addition of the zinc, as it combines with the zinc more readily than does silver.

Work-lead gives after desilvering the following products :

0·35 per cent. cakes from melting, with an average contents of 0·0004 per cent. gold and 0·10 per cent. silver,

2·25 per cent. rich scum for distillation, with an average contents of 0·0153 per cent. gold, 4·0510 per cent. silver, 53·2 per cent. lead, 2·68 per cent. copper, and 39·7 per cent. zinc; that is :

- 1·73 per cent. of rich scum I. with 0·0174 per cent. gold, and 4·670 silver,
- 0·31 per cent. rich scum II. with 0·0016 per cent. gold, and 2·53 silver,
- 0·21 per cent. rich scum III. with a trace of gold, and 1·130 per cent. of silver,

besides 98·95 per cent. of zinkiferous poor lead for de-zinking with an average contents of 0·0007 per cent. of silver and 0·75 per cent. zinc.

There are returned to the process : 1·5 per cent. eliquated lead, containing on the

average a trace of gold, 0·032 per cent. silver, and 1·3 per cent. zinc. Poor scum is not formed because the zinc-scum obtained after the third addition of zinc gives on eliquation the above rich scum III., containing a moderate amount of silver and capable of useful distillation. The quantities of the eliquated rich scum increase with the proportion of silver in the work-lead, and the silver in the rich scum increases proportionally, whilst the lead in the normal case of eliquation remains at a limit of 76–80 per cent. and the zinc remains between 20–24. The quantities of poor scum remain approximately equal in all sorts of work-lead, since the silver reduced in them by repeated additions of zinc shows the essential variations, if the poor scum is drawn off. The lead reaches, as a maximum, 90 per cent. and the zinc 6–9 per cent. The yield of eliquated lead, with uniform management, keeps step with the quantities of rich scum, and must increase or abate in a corresponding proportion, according as more or less rich scum is taken off in consequence of the higher or lower proportion of silver in the material. The silver in eliquated lead is uniformly moderate, since the main quantity of the silver is kept back by the zinc remaining in the eliquated rich scum, and the small quantities of silver in the eliquated lead are carried over only by the zinc, which passes in. The zinc fluctuates between 1 and 1·5 per cent. The zinkiferous poor lead, if the process has been duly conducted, shows a constant proportion of 0·75 per cent. of silver, whatever quantities of zinc were required for desilvering the work-lead. The total gold and copper of the work-lead will be found taken up in the rich scum, so that all subsequent products are free from these two metals.

For the subsequent de-zinking in the refining furnace, the zinkiferous poor lead which has gone down in temperature by removal from the desilvering-pan to the refining furnace must be heated to, and maintained at, redness. There is soon formed by the oxidising influence of the blast upon the surface of the lead-bath a film of lead and zinc oxide, as a thin crust which must be drawn off with a crutch through the working doors to keep the surface of the lead clean. This drawing off the films must continue until pure litharge appears as the product of oxidation, when the de-zinking process is at an end. The tap-hole in the refining furnace is then opened and the lead is run off into the poor lead pan, which has been heated in the meantime. When the cake floating upon the surface has been lifted off, the lead is finally run out through the escape pipe at the bottom of the pan, and let off into iron moulds as the pure lead of commerce. If two desilvering pans are worked simultaneously, the de-zinking can at once begin in the refining furnace as soon as the former lot has been let off into the poor-lead pan.

The films from the refining furnace and the lead-scum from the poor lead pan, as soon as a sufficient quantity has been collected, are first returned to the refining furnace, in order to smelt out of them a not unimportant quantity of lead, and then, much reduced in weight and volume, they are used as a plumbiferous addition in the treatment of the ore. The refiner's films, when ground, form a good pigment for varnish-painting, and may thus be partially disposed of. The poor lead yields 94·2 per cent. commercial lead and 6·17 per cent. of refinery scum. The total de-zinking process from running the poor lead into the refining process to letting off the de-zinked lead requires a mean of nine hours. The original proportion of zinc (0·75 per cent.) in the zinkiferous poor lead is reduced in three hours to 0·16, in five hours to 0·01, in seven hours to 0·0008, and in nine hours to 0·0002 per cent.

For distilling the rich scum it is mixed (after being kept as clean as possible) with 1 per cent. of coarse charcoal powder; the bottom of the graphite crucible is then covered with a thin layer of pieces of charcoal of the size of a walnut, and the crucible is then filled up to the rim with rich scum. The cover, *h*, coated at its edge with a moist lute (of 1 part clay, 1 part ground tiles, and 1 part ground coke) is placed upon the crucible, connected with the receiver *k* (Fig. 187), and the furnace is filled with

coke. When the distillation is at an end the receiver, containing the zinc which has passed over in the shape of a lump, is moved away, the grate of the wind-furnace is freed from slag and ashes, the ring and cover of the shaft are drawn away, and the lid of the crucible is taken off as quickly as possible, since when cold it adheres fast to the crucible and cannot be removed without the risk of breakage. As soon as the crucible has ceased giving off fumes, the residue of the charcoal and the unreduced scum floating on the surface of the separated rich lead are lifted off by means of a perforated ladle, and the rich lead itself is baled out into cast-iron pans. After this is completed, a small quantity of charcoal is again laid at the bottom of the crucible, and a fresh lot is introduced. From the rich scum are obtained :—

57·17 per cent. rich lead, containing 0·0186 per cent. gold, and 7·35 per cent. silver,
5·85 per cent. crucible scrapings, containing 0·0112 per cent. gold, 4·608 per cent. silver, and 3·5 per cent. copper,
29·54 per cent. metallic zinc,
6·35 per cent. zinc in 7·22 per cent. zinc-dust and scrapings.

With careful working, 50 per cent. of the zinc run over can be recovered, which completely covers the costs of distillation.

From a work-lead containing 0·84 per cent. of auriferous silver there are obtained (without reference to losses of metals on Pattinsonising) with 16 pans :—

Rich lead	41·0 per cent.
Commercial lead	49·0 „
Lead in intermediate products	10·0 „

The first of these items contains 2·0 per cent. of gold and silver, the second 0·001 and the third 0·2.

Of the gold and silver there are found !—

96·6 per cent. in the rich lead,
0·1 „ in the commercial lead,
2·3 „ in the intermediate products.

On Pattinsonising with nine pans, and treating the lead on the Parke process :—

Rich lead	38·9 per cent.	with 2·14 per cent.	}	Gold and silver.
Commercial lead . . .	52·5 „	0·001 „		
Lead in intermediate products.	8·6 „	0·18 „		

Of the gold and silver there occur :—

99·1 per cent. in the rich lead,
0·1 „ in the commercial lead,
0·8 „ in the intermediate product.

This latter procedure is therefore more remunerative than the former.

Desilvering Work-Lead by Electricity.—The electric refining of silver still occasions difficulties. It is a hindrance that neither lead nor silver forms firm, sheet-like deposits, but mostly dendritic concretions. Experiments for producing soft lead electrolytically show that the difference of price between the two qualities does not at present open a prospect for the electric process.

Fine-burning Silver.—Silver as directly obtained from its ores, whether by amalgamation, or by lead-work, or by precipitation from its solutions by means of metallic copper, still contains several per cents. of other metals. The process on the refining hearth is never continued long enough for the complete oxidation of all other metals, and the actual quantity left in the sample on brightening is sometimes as much as 9·5 per cent. The purification of silver from all admixtures of other metals is called fine-burning. If lead is present or forms the chief ingredient of the contaminating matters the fine-burning is simply a prolonged refining conducted not on the large hearth of the refin-

ing furnace but in a smaller space. If lead does not preponderate among the impurities, the silver receives an addition of lead before the oxidation is begun. Small quantities of litharge are always produced in the process, but they are not allowed to run off from the surface of the silver, but are absorbed by the mass (bone-ashes, marl) of which the apparatus used in fine-burning is composed. We distinguish three kinds of fine-burning, *i.e.* (1) in capsules or iron rings; (2) in the muffle; (3) in the reverberatory, the last process is the simplest and most advantageous.

The production of gold and silver in the world in 1884 was:

	Gold. Kilos.		Silver. Kilos.
Germany	555	...	248,115
United States	46,343	...	1,174,205
Russia	32,829	...	9,336
Australia	42,960	...	2,788
Mexico	1,780	...	655,868
Austrian Empire	1,658	...	49,424
Sweden and Norway	19	...	8,203
Italy	109	...	432
Spain	—	...	3,562
Turkey	10	...	2,164
La Plata	118	...	10,109
Columbia	5,802	...	18,286
Bolivia	109	...	384,985
Chili	245	...	128,106
Brazil	952	...	—
Japan	256	...	21,121
Africa	3,000	...	—
Venezuela	5,022	...	—
Canada	1,435	...	1,641
France	—	...	6,356
Peru	179	...	45,909
	143,381	...	2,770,610

According to Soetbeer the total production of the world between the years 1493 and 1875 was:

	Silver. Kilos.		Gold. Kilos.		Value in million shillings.
Germany	7,904,910	...	—	...	1,422·9
Austria	7,770,135	...	460,650	...	2,683·8
Rest of Europe	7,382,000	...	—	...	1,328·8
Russia	2,428,940	...	1,033,655	...	3,321·1
Africa	—	...	731,600	...	2,041·2
Mexico	76,205,400	...	265,040	...	14,456·4
New Granada	—	...	1,214,500	...	3,388·5
Peru	31,222,000	...	163,550	...	6,076·3
Bolivia	37,717,600	...	294,000	...	7,609·4
Chili	2,609,000	...	263,000	...	1,205·1
Brazil	—	...	1,037,050	...	2,893·4
United States	5,271,500	...	2,026,100	...	6,601·7
Australia	—	...	1,812,000	...	5,055·4
Otherwise	2,000,000	...	151,000	...	783·0
	180,511,485	...	9,453,345	...	58,857·0

Of this total value silver amounts to 32,492 and gold to 26,375 million (shillings).

Chemically pure silver is obtained by dissolving cupriferous silver in nitric acid, precipitating the silver from the solution by means of sodium chloride or hydrochloric acid, and reducing the silver chloride by introducing it into melting potassium carbonate or igniting it with resin and potash. Silver chloride is reduced in the moist way by bringing it in contact with zinc and dilute hydrochloric acid:—$AgCl_2 + Zn = ZnCl_2 + Ag$.

Gutzkow prepares fine silver by placing silver sulphate in a hot solution of ferrous sulphate, when ferric sulphate and metallic silver are formed: $AgSO_4 + 2FeSO_4 = Fe_2(SO_4)_3 + Ag$, which is washed, dried, and smelted.

Pure silver has a pure white colour and a strong lustre which is much heightened by polishing. It is softer than copper, but harder than gold. It is extremely ductile and malleable, in which respect it exceeds all other metals except gold. Very small admixtures of some metals decrease its ductility and malleability; the presence of copper, however, is not injurious, and that of gold is even beneficial. An admixture of lead, antimony and selenium is very pernicious. If melted with charcoal, silver loses its flexibility, but it may be melted in a graphite crucible without any change in its properties. The sp. gr. of silver is 10·5; by hammering it may be increased to 10·62. At very high temperatures silver is volatilised. If melted with access of air, silver absorbs oxygen, which as the metal solidifies escapes often with a noise and with the projection of liquid silver (spitting, or spirting). If silver contains a trace of lead or 1 per cent. of copper it solidifies quietly with a concave surface, as when cold it occupies a smaller volume than when melted. It is not attacked by weak acids but dissolves in nitric acid in the cold, and in strong sulphuric acid with the aid of heat.

Silver Alloys.—Silver forms alloys with lead, zinc, aluminium, bismuth, tin, copper, gold, and other metals, of which that with lead is important in the extraction of silver. The most useful of its alloys are those with copper, since pure silver is too soft and is scarcely ever wrought except alloyed with copper. The alloys are harder than silver.

The German silver coins contain 0·900 of fine silver; the ore of the Latin monetary union 0·900 and 0·835, those of Britain 0·925.

Silver Assay.—In order to ascertain the fineness of an alloy, presuming that it contains nothing but silver and copper, we may proceed (1) by the dry way, cupellation; or (2) by the moist way, titration; or (3) by the hydrostatic method.

The process of cupellation requires too many niceties to be here adequately described. The reader is, therefore, referred to: *Mitchell's Manual of Practical Assaying*, 6th edition, edited by W. Crookes, F.R.S., pp. 601–634.*

The assay by the moist way, the titration method of Gay-Lussac, is more easily executed and is accurate to $\frac{1}{200}$ = ·5 per cent. Since it is known that 5·4274 grammes of sodium chloride precipitate exactly 1 gramme of silver from solution, the fineness of a dissolved alloy can be found by the use of the ordinary apparatus for titration.

Volhard uses for precipitating silver from an acid solution mixed with a little ferric sulphate, ammonium sulphocyanide. As soon as all the silver is deposited as a sulphocyanide, the red colour of iron sulphocyanide appears.†

For cases in which cupellation and titration are not admissible Karmarsch recommends a hydrostatic assay in which the proportions of copper and silver are determined by specific gravity. As copper and silver expand when alloyed, but alloys become the denser the more they are exposed to mechanical pressure, there is here an uncertainty in the very basis of the hydrostatic silver assay which renders it inapplicable for silver which has been cast and subsequently worked, but only for silver coins.

Silvering.—Silver-plating, or the coating of other metals with silver, can be effected (1) by plating; (2) by fire (fire-silvering); (3) in the cold way; (4) in the wet way, and (5) galvanically. In order to cover sheet-copper with a layer of silver the surface of the copper is carefully cleaned and moistened with a solution of silver nitrate, which produces a thin film of silver. Upon this film there is laid a plate of silver; both are heated and extended between rollers. Copper wire may be silvered by simply laying sheet silver upon it and passing it, hot, through grooved rollers.

Silvering in the fire is effected by means of a silver-amalgam or a mixture of 1 part

* See also *Select Methods in Chemical Analysis*, by W. Crookes, F.R.S., p. 359.

† See also Mitchell's work above quoted, pp. 634—685; and *Select Methods*, p. 286.

precipitated silver, 4 parts sal-ammoniac, 4 parts sodium chloride, and ¼ part of mercuric chloride, which is rubbed upon the surface of the metal previously well cleaned. The mercury is then expelled from the coating of amalgam by ignition. For silvering buttons there is used a paste of 48 parts sodium chloride, 48 parts zinc sulphate, 1 part mercuric chloride, and 2 parts silver chloride.

For silvering in the cold the cleaned surface of the metal to be silvered is rubbed by means of a cork with a mixture of equal parts silver chloride and sodium chloride, ⅔ parts chalk, and 2 parts potash moistened with water, until the colour of silver is produced as desired. According to W. Stein 1 part silver nitrate and 3 parts potassium cyanide are rubbed together with water enough to form a thick paste, which is quickly and uniformly rubbed on with woollen rags. To silver iron it must first be coated with a layer of copper.

In silvering in the wet way the metal to be coated is placed in a boiling solution of equal parts of tartar and common salt with ¼ silver chloride until the silvering is sufficient.

For galvanic silvering (electro-plating), recently precipitated and well-washed silver chloride is introduced into a solution of potassium cyanide (100 grammes cyanide to one litre water), as long as it is taken up, and to this solution is added an equal measure of solution of potassium cyanide.* Galvanic silvering is applicable upon copper, bell-metal, brass, pinchbeck, cast- and bar-iron. Tin, zinc, and polished steel must be previously coated with copper, if the silver is to be permanent. Articles made of German silver, and Britannia metal, and electro-plated, known under the names of "Alfenide" or China silver, occur in commerce, and have been already mentioned. Upon one square metre of metallic surface there are deposited from 1 to 22, and even 240, grammes silver, so that the thickness of the stratum of silver varies from $\frac{1}{9400}$ to $\frac{1}{540}$, and even $\frac{1}{42}$, of a millimetre. Galvano-plated articles sometimes further receive a slight coating of palladium to preserve them from being blackened by the action of hydrogen sulphide.

The black colouring of silver articles, sometimes in vogue, and called the oxidation of silver is produced either by sulphur or by chlorine. The former agent gives a blue-black tone, and the latter a brownish black. To obtain the sulphur colour the articles are immersed in a solution of potassium sulphide. For the chlorine colour the silver must be immersed in a solution of copper sulphate and sal-ammoniac.

GOLD.

Occurrence.—Almost exclusively metallic, either *in situ*, in quartz rock, especially along with quartz, pyrites, and hydroferrite; also as gold-sand, in dust or grains, leaflets, and rounded pieces (nuggets), in the sands of rivers or in alluvial soils, consisting chiefly of clay and quartz-sand along with mica, water-worn fragments of syenite, chloritic slate, grains of chrome iron and magnetic iron, spinel, garnet, &c. In the metallic state it always contains more or less silver, as electrum. According to recent analyses, native gold contains :

	Transylvania.	S. America.	Siberia.	California.	Australia.
Gold	64·77 ...	88·04 ...	86·50 ...	90·60 ...	99·2 and 95·7
Silver	35·23 ...	11·96 ...	13·20 ...	10·06 ...	0·43 „ 3·8
Iron and other metals .	— ...	— ...	0·30 ...	0·34 ...	0·28 „ 0·2

Gold is also often met with in native tellurium and silver telluride, sometimes in argyrythrose and proustite, in iron pyrites, copper pyrites, in stibine, in blende, in arsenical pyrites (*e.g.*, that of Reichenstein in Silesia) and galena. The chief supplies

* The most useful form of battery for depositing silver is a modification of the Wollaston battery. For the details of the process, and for methods of producing dead or bright surfaces at pleasure, the reader may consult *Electro-deposition of Metals*, by A. Watt (Crosby Lockwood & Co.).

of gold are obtained from the Ural, the United States (California, Nevada, Arizona, Montana, Utah, and Colorado), from British Columbia, Nova Scotia, Mexico, Peru, and Brazil, from Australia (especially Victoria, New South Wales, and Queensland), Tasmania, New Zealand, and in Africa (Natal, the Transvaal, &c.). The Ural Mountains and Siberia also yield much gold.

The gold deposits of India (the Wynaad and elsewhere) must in earlier ages have yielded a large part of the treasures of Eastern kings, but in modern times their working has not proved very remunerative. In the British Islands gold was formerly obtained in considerable quantity. The placer mines of Croghan Kinshela, in county Wicklow, were worked about the beginning of the present century. In 1795, a large nugget, weighing 21½ oz., was picked up at the ford of Ballinasilloge, in a stream since known as the Gold Mines River. The Government placers yielded 944 oz. of gold, whilst over £10,000 were paid for gold sold by private individuals. Geological authorities consider it probable that vast quantities of auriferous sands still exist untouched under the deep river accumulations in the valley of the Ovoca.* The South of Scotland at one time produced gold, *e.g.*, the head waters of the Clyde, Tweed, and Annan. The specimens lately obtained have served merely as curiosities. In Sutherland gold-seeking was commenced in the years 1867 and 1868, and a certain amount of the precious metal was found, but as all the works have been abandoned, the operations cannot have proved remunerative. In North Wales, especially Merionethshire, the result is of greater importance. A Welsh mine owner is known to have lent Charles I. £500,000 in Welsh gold at the beginning of the Civil War. Latterly and at present mining is carried on in the Cefn Coch and Gwynfynydd mines. Some of the lode-stuff raised gives 87 oz. per ton, but owing to the sulphuretted character of the mineral no known method of working has proved fully successful.†

In the earlier days of all auriferous districts, gold was obtained in dust, grains, scales, and nuggets, derived from the weathering of gold-bearing rocks and found in shallow diggings in alluvial soils (placers), or procured by washing the sands of river-beds or the deposits of floods. If such matter is dexterously washed and shaken, the gold grains sink to the bottom on account of their superior gravity. The more minute particles are, however, in such cases lost.

When water is plentiful the gold alluvium is washed by means of strong currents, which wash the mud, sand, and shingle into large sluices, in which the particles of gold sink to the bottom. This method involves, however, greater losses than washing by hand or by machinery. In any case when the placer diggings and the washings in a district are exhausted, the next method is grinding up the gold-quartz in specially constructed mills. As it exists in particles often finer than flour, it has to be extracted from the mass by means of mercury, either incorporated with the ground ore, or presented in the form of amalgamated copper plates, which are fixed obliquely in the long troughs in which the ore is ground up with water. From time to time these plates are lifted out and scraped, and returned to the troughs after being re-amalgamated.

There is, however, a distinction to be made in the character of gold-bearing quartz. In some kinds—the "free-milling" sorts—the gold is easily, and, if the mechanical arrangements have been properly constructed, completely taken up from the ground mineral. Such free-milling quartz generally lies near the surface, where the rocks are permeated by atmospheric air and water, and where consequently, in the lapse of ages, the base metals and their compounds have been oxidised, decomposed, and washed away, leaving the gold free. As the miner penetrates deeper he comes upon minerals

* See Kinahan, *Quarterly Journal of Science*, April 1878, N. S., vol. viii. p. 289.

† For details the reader is referred to a paper on "British Gold," by R. Hunt, F.R.S., *Quarterly Journal of Science*, 1865.

situate below the permanent water-line.* Here the gold cannot be readily extracted by the amalgamation process, as it exists, if not combined, at least entangled among blende, arsenical pyrites, galena, and antimony ores, so that it to a great extent escapes the action of the mercury. Hence the gold actually extracted from a mineral in practical working falls sadly short of the quantity found on assaying. Very small quantities of lead, copper, arsenic, or antimony quickly spoil the mercury, and render it unable to take up the gold. Among the most successful expedients for combatting this evil, ranks the use instead of pure mercury of sodium-amalgam as invented by W. Crookes, F.R.S.

The presence of sodium keeps the mercury bright and active. This compound is prepared in three modifications A, B, and C. Amalgam A is a combination of 3 parts sodium with 97 of mercury. The mixture is prepared as follows :—A strong iron flask with a narrow neck is bedded nearly up to the mouth in a sand-bath at 198° ; the materials are weighed out, the mercury is poured into the flask, and the sodium is dropped in, taking pieces of the size of a pea each time, and using an iron forceps. The action should be allowed to cease each time before a fresh portion is added. When the whole of the sodium has been introduced, the amalgam is poured, whilst still liquid, into a flat iron dish, and when cold is broken up and kept in a stoppered jar. Amalgams B and C contain an addition of zinc, and are recommended for use.

Both from experiments and from practical working,† it appears that when sodium-amalgam is used according to the instructions of the inventor, and is not expected to dispense with all judgment on the part of the operator, it greatly facilitates the amalgamation of gold, which, it must be remembered, is not so easily taken up by mercury as it is commonly believed.

Mr. W. Skey, analyst to the Geological Survey of New Zealand,‡ finds that numerous samples of bright, clear-looking gold, of all degrees of fineness, refuse to amalgamate on any part of their natural surfaces though taken direct from the reef and untouched by hand; that on such surface sulphur is always present; that native gold or gold in a pure state readily takes up sulphur from moist sulphuretted hydrogen or ammonium sulphide and absorbs it directly when administered in boiling water; that surfaces so treated refuse to amalgamate, though no apparent change can be observed; gold so affected is rendered amalgamable by roasting in an open fire, except copper is present to the extent of 7 per cent. or perhaps less, whilst the same effect is produced by contact with potassium cyanide, chromic and nitric acids, and chloride of lime acidified. The author is of opinion that this absorption is of a chemical character. He has observed that iron sulphates in presence of air and water decompose various metallic sulphides common in gold reefs, liberating sulphuretted hydrogen. He has also proved that the action of sulphuretted hydrogen renders gold non-amalgamable, and he suggests that much of the loss in extracting gold from auriferous minerals of amalgamation depends on the presence of a thin film of sulphurised gold which envelops the particles.

An immense quantity of gold is lost by being carried away in the form of tailings too fine to be deposited in any practicable time. It is estimated that though the State of California since 1848 has produced gold to the value of £250,000,000, yet more "has been wasted in milling and hydraulic mining by being washed down the rivers and even to the ocean." An experienced Californian expert, quoted by Eissler, states that in his experiments "gold has been taken up in distilled water so fine that it could not precipitate in less than from five to ten minutes." Gold of this character obviously cannot be saved in running streams.

* See Eissler's *Metallurgy of Gold*, Crosby Lockwood & Co.

† See Ure's *Dictionary of Arts, Manufactures, and Mines*, Longmans, vol. ii. p. 697.

‡ *Chemical News*, vol. xxii. Dec. 9, 1870, p. 282.

Great care must be observed in the "milling" process. If the ore is too coarse, a proportion of the gold is certainly wasted, as many of the particles remain incrusted with silica, and never come into actual contact with the mercury at all. On the other hand, if the ore is crushed too fine, much of the gold will float instead of amalgamating, and is not arrested either by the amalgamated copper or silver plates, or by the "blankets" suspended in the sluices. The pulp is generally caused to flow over three sets of blankets. The first set are washed every twenty minutes, and the second every two hours.

A so-called hydrogen amalgamation process—perhaps more correctly styled an electric process—has been patented by Molloy, and is being worked in America by the Hydrogen-Amalgam Company. The apparatus used consists of a shallow pan, 1 inch in depth and 41½ inches in diameter, containing mercury to the depth of half-an-inch. In the centre of this pan is a porous jar, so fixed that the mercury cannot enter or displace it. Within the jar is a cylinder of lead and a solution of sodium sulphate. This lead cylinder forms the anode, and is coupled with the positive pole of a small dynamo, whilst the mercury is connected with the negative pole of the same machine. As the current passes, hydrogen is evolved from the surface of the mercury, which combines with a portion of it, forming a hydrogen-amalgam. According to the statements of the Hydrogen-Amalgam Company, quoted by Eissler, this process prevents the mercury from turning "sick" (losing its activity), and effects an increased yield of gold amounting to 10 per cent. at the expense of only threepence per ton for electrical and mechanical force and labour.

To obviate the waste of gold and mercury and the losses involved in the ordinary processes, Mr. W. Pritchard Morgan, M.P., and Mr. J. Needham Longden of Sydney, have invented and patented a dry amalgamation process, in which water is entirely dispensed with. This is in itself no small advantage in many parts of Australia and Africa. The ore is first comminuted, not by grinding or stamping, but by the "Jordan" pulveriser, which acts nearly in the manner of a Carr disintegrator, and reduces the mineral to a powder, passing it through a sieve of 8100 meshes to the square inch, or forty times as fine as is commonly done. This, in a wet process would be fatal, as it would allow much of the gold to float, but where water is not present it is an advantage, as it secures the contact of the gold with the mercury. The mercury is applied dry and hot by means of a self-acting apparatus which ensures perfect contact but which cannot be described intelligibly without the aid of a working model. As the process is completed the ground ore is forced into the concentrating chamber. Messrs. Jordan, Son & Comman, of Gracechurch Street, erected plant for the process at Stratford Market, and found a considerably increased yield of gold with a *decrease* of the working cost. It is needless to say that this process can be worked with sodium amalgam, which, in the presence of antimony, would be found advantageous.*

The following method of treating refractory gold ores, sulphides, tellurides, arsenio-sulphides, &c., containing zinc, copper, iron, bismuth, and antimony has been devised by W. Crookes, F.R.S. The object sought is to prevent the flouring and sickening of the mercury and the tarnishing of the gold grains, which together involve a loss of from 20 to 80 per cent. of the gold present as found on assay. Various methods for preventing these evils have been suggested, but none of them have proved satisfactory. Mr. Crookes submits the ores, tailings, sulphides, etc., to the joint action of a solution of mercury cyanide, or of some other soluble salt of mercury, and of an alternating electric current. The ore in question is reduced to a powder in the usual manner, mixed with a solution of sulphate, nitrate, chloride, or cyanide of mercury, and a rapidly alternating current of electricity is then passed through the mass either when

* For further particulars, the reader is referred to the *Journal of Science*, Third Series, vol. vi. (1884) p. 416.

at rest or when kept in a state of agitation. The bulk of the mass is not a very good conductor of electricity, whilst the fine particles of gold disseminated through the mass are excellent conductors. The poles may be made of iron or carbon, each being alternately anode or kathode. Each alternation of the current causes mercury to be precipitated on alternate surfaces of the particles of gold in the mass of ore, without requiring the gold to be in metallic communication with either pole. The sizes of the particles are not material, as the finest "flour" and "float" gold will be amalgamated and thus weighted as well as the largest pieces.

An advantage incidental to the use of an alternating current is that the sudden and the violent decompositions and recompositions alternating with great rapidity cause the mass to become warm, thus greatly facilitating the decomposition. The efficient action of the alternating current depends on the right adjustment of several variable factors, *e.g.* (1) current density; (2) area of electrodes; (3) rate of alternations per second; (4) electric conductivity of the wet mixture of crushed ore and liquid. As this last factor varies with every kind of ore the others will have to be adjusted in each separate case to get the maximum effect. Hence no general directions can be given.

If it is impracticable to use an electric current the inventor employs a solution of mercury cyanide or sulphate, either of which will superficially amalgamate the particles of gold, though less rapidly than with the aid of the alternating current. The reaction may be hastened somewhat by heating the mass.

When carrying out the process in this manner the inventor uses a solution of 2 or 3lbs. of mercury cyanide or sulphate, dissolved in 80 to 100 gallons of water.

In some cases he finds it advantageous to add to the mercury used in the subsequent amalgamation process a little sodium amalgam as described in his specification No. 391 of 1865 or some of the modified amalgams described in his specification No. 2229 of 1865.

The points here claimed are the improvements in amalgamating and extracting gold, which consist in submitting the ore to the joint action of a solution of mercurial salt and an alternating electric current. Further, the improvement in amalgamating and extracting gold, which consists in submitting the ore to the action of a solution of mercury cyanide or sulphate, and lastly the improvement in the final amalgamating process by using a solution of cyanide or sulphate of mercury, or an alternating electric current, in conjunction with a solution of a mercurial salt.

The extraction of gold from gold-sands may be effected completely by fusion. The sand is smelted with iron ore in blast furnaces with suitable fluxes, thus yielding auriferous raw iron, from which the gold is subsequently extracted by means of sulphuric acid. If gold is present in copper or lead ores they are roasted and washed. Auriferous sulphides are sometimes roasted and smelted. The raw stone or matte thus obtained is again roasted, melted afterwards along with litharge, which takes up the gold present in the matte, and is separated on the refining hearth.*

Plattner devised a process for extricating gold from its minerals by means of chlorine; it has been improved by Deetkin, Kustel, Bruckner, Mears, and others. The process of chlorination consists, generally speaking, of the following operations :—

(1) The comminuted auriferous matter is perfectly oxidised, moistened with water, and sifted into a wooden vat, coated with tar or resin and having a perforated false bottom. It is then covered with a lid, which must fit well. Chlorine is liberated below the false bottom, whether from a mixture of salt, pyrolusite, and sulphuric acid, or from chloride of lime in contact with an acid, and allowed to penetrate the mass of ore from below. When the chlorine has pervaded the entire mass, the vat is closed at the top, and allowed to stand for a few hours covered up. The lid is then removed and water is added so as to fill it up on a level with the top of the ore. It is found that

* This process has not come into general use in America or Australia.

the gold has been converted into a soluble terchloride, which is dissolved out with water. Lastly, a solution of ferrous sulphate is added to the clear liquid, when the gold is thrown down as a black or brown precipitate, which is collected, washed, and melted down.

As a condition for success, sulphuretted ores must be carefully roasted before chlorination, as must also be all minerals containing lead, beginning at a very low temperature. Sulphates, if present, must be destroyed by roasting. No hydrochloric acid gas must accompany the chlorine: hence in many cases it is advisable to generate chlorine in a separate vessel, so that it may be washed in pure water before it is introduced below the false bottom.

In the modification of the chlorine process devised by M. Their the chlorinator is an iron barrel lined with lead, with a man-hole at one side for filling and emptying. A ton of ore is introduced at a time, the barrel is partially filled with water; about 20 lbs. of chloride of lime are introduced, followed by the roasted ore, and the proper quantity of sulphuric acid—about 25 lbs. The man-hole is tightly closed, and the barrel is caused to revolve until the gold is dissolved, which is generally effected in six hours. The contents of the barrel are then rinsed out upon a filter.

For a full account of the various modifications of the chlorination process, of the precautions required, and the utilisation of silver and other matter present, see Eissler's work above-mentioned (chapters vi. and vii.).

The gold, as obtained by whatever process, contains small admixtures of other metals, always including silver. The gold may be separated—(1) By antimony sulphide; (2) by sulphur and litharge; (3) by chlorine; (4) by the quartation process; and (5) by sulphuric acid.

In the process of parting by antimony sulphide, the alloy of gold (containing at least 60 per cent. of gold) is melted in a graphite crucible, and pulverised antimony sulphide is then introduced. The melted mass is poured into an iron mould. When cold, the mass is found separated into two layers, the upper, or plagma, consisting of silver, copper, and antimony sulphides; and the lower, being the regulus (gold antimonide). The latter is then roasted, and the residue of gold is melted with borax, saltpetre, and powdered glass.

The operation with *sulphur* is a concentration, preparatory for separation in the wet way, especially for quartation, the object being only to economise nitric acid. The granulated alloy of gold is put in an ignited graphite crucible, along with one-seventh part of powdered sulphur, and covered with powdered charcoal. It is kept first for two to two and a half hours at a low red-heat, and is then heated to fusion. If the alloy contained considerable proportions of gold, there is separated out a silver rich in gold, whilst but little gold remains in the plagma. If the alloy was poor in gold, such a separation takes place very imperfectly, or not at all. To effect this, litharge is sprinkled upon the melted mass; its oxygen converts a part of the sulphur into sulphurous acid, whilst the liberated silver is eliminated along with the greater part of the gold.

For separating gold by means of chlorine the auriferous alloy, in fine grains or in thin sheets, is stratified in a crucible, with so-called cement powder (consisting of 4 parts ground bricks, 1 part common salt, and 1 part ignited iron sulphate), and exposed for several hours to a gradually increasing heat. By the action of the ferrous sulphate upon the salt, chlorine is liberated, which converts the silver into chloride, but does not attack the gold. The silver chloride is absorbed by the ground bricks. When cold, the mass is boiled in water to recover the gold. In 1869 Miller founded upon the property of chlorine not to attack gold at elevated temperatures a new process for purifying gold, which has been successfully introduced at the Mints of London, Sydney, and Philadelphia. Chlorine gas is introduced into the melted metal through a stoneware pipe, and combines with the silver to form silver chloride, which

rises to the surface of the melted gold; the gold remains perfectly desilvered. Instead of chlorine gas, bromine may be used.

Separation in the wet way, or quartation, derives its name from the traditional assumption that in order to separate gold from silver in this manner the latter metal must amount to three times the quantity of the latter. Pettenkofer has shown that two parts of silver are sufficient if the acid is sufficiently strong, and the boiling is duly prolonged. For this purpose the alloy is melted up with the needful quantity of silver, the mixed metal is granulated and covered in a platinum pan with nitric acid of sp. gr. 1·320, perfectly free from chlorine. Silver is dissolved, whilst the gold remains, and is melted in a crucible with borax and saltpetre. The silver is thrown down from the solution by means of copper or zinc.

The separation of gold by means of sulphuric acid is preferable to quartation, on account of its simplicity and cheapness. The separation is effected most readily if the alloy contains in 16 parts not much above 4 and not much less than 3 parts of gold. The sulphuric acid used in the process must have the sp. gr. 1·848. The alloy is placed in a suitable pan, and covered with sulphuric acid and heated. In twelve hours the silver and the copper are completely dissolved:—

$$AuAg_2 + 2H_2SO_4 = Au + Ag_2SO_4 + SO_2 + 2H_2O.$$

When all the silver and copper are converted into sulphates, the solution is poured into a leaden pan, and the silver sulphate, which congeals to a crystalline paste, is taken out with an iron shovel and put in lead pans filled with hot water. The precipitation of the sulphate is effected with slips of sheet-copper. The solution of copper sulphate is neutralised as completely as possible with copper oxide, and worked up as copper sulphate. The gold which remains undissolved is freed from accompanying ferric oxide, copper sulphide, and lead sulphate, by boiling with sodium carbonate and treatment with nitric acid, dried, and remelted with a little saltpetre. This method of separation has rendered it possible to refine to advantage old cupriferous silver containing $\frac{1}{10}$ or $\frac{1}{12}$ per cent. of gold, as is often the case in old silver coins.

According to Gutzkow's proposal, there are worked up: gold ingots from California, set at 2 parts gold and 3 parts silver and then granulated; silver ingots from the Comstock mine, containing 2 to 10 per cent. of gold, which are dissolved up at once without granulating; and, finally, silver in the form of bricks containing a considerable proportion of copper from the amalgamation of the tailings, and from the mines of Nevada. These bricks are smelted with so much fine silver that the proportion of copper is reduced to 8 per cent.

There is used for dissolving the alloys a cast-iron pan, 66 centimetres in width and 45 centimetres in depth, made more capable of resisting acids by containing 2 to 4 per cent. of phosphorus. It takes a charge of 100 to 150 kilos., which is introduced through an opening in the dome capable of being closed with a slide. The gases and vapours given off during dissolving are passed through a leaden pipe into a chamber lined with lead plates, and from here through a tower into a lofty chimney. The sulphuric acid put in at 168° Tw., is heated to a boil, and the alloy is added. The hot solution, floating above the undissolved gold is syphoned off into a deep iron receiver, through an iron pipe into sulphuric acid at the heat of 110°, and of the strength of 123° Tw. Of this 1 cubic metre is required for every 200 kilos. of the alloy treated; it is obtained as a mother-liquor on the crystallisation of silver sulphates. As the liquid cools, silver sulphate crystallises out, whilst copper sulphate remains in solution. Upon the silver sulphate crystals a hot, saturated neutral solution of ferrous sulphate is conducted, which first dissolves copper sulphate, then reduces the silver sulphate, takes up the free acid, and flows off, at first as a blue and then as a brown liquid, until a green colour indicates the end of the reduction. The blue cupriferous liquid is preserved separately from the brown liquid, in which there are still in

solution 2·5 per cent., of silver. The reduction is complete in 3 to 4 hours. The solution of ferric oxide is re-converted into a ferrous salt by the addition of waste iron.

Chemically pure gold is obtained by dissolving gold in *aqua regia;* the solution is separated from silver chloride, &c., by filtration; the filtrate is evaporated to dryness, the remaining gold chloride is taken up in water, and the gold is precipitated by a solution of ferrous sulphate: $2AuCl_3 + 6FeSO_4 = 2Au + 2Fe_2(SO_4)_3 + Fe_2Cl_6$.

Properties.—Gold is yellow, but very small traces of other metals can modify its colour. It takes a very high polish. In hardness it is little superior to lead, but it is the most malleable and extensible of all metals. It possesses an absolute solidity almost equal to that of silver. Its elasticity is unimportant, whence it is but little sonorous. Its sp. gr. varies from 19·25 in the cast and unextended state, to 19·55, and even to 19·6, when it has been condensed by mechanical manipulation. Gold fuses at 1037° Deville, 1075° Erhard, and after casting it contracts strongly in the mould. Melting gold shines with a sea-green colour. Its value is much increased by the fact that it remains unaffected in the air, in sulphuretted gases (see Skey's observations, p. 190), in water, and in contact with all acids, except aqua regia.* Of all metals gold has the greatest tendency to combine with mercury. In thin leaves it is translucent with a blue or a green light according to its degree of tenuity.

Gold Alloys.—Fine gold is not used in the arts on account of its softness; it is employed only for (genuine) leaf gold, and for ornamenting glass and porcelain. Its standard of fineness is expressed in this country in carats. Absolutely pure gold is said to be 24 carats fine. An 18-carat gold is understood to contain 18 parts of fine gold and 6 of copper or silver. The alloys containing copper have a more reddish and those containing silver a more whitish yellow colour.

The quantity of gold used in ornamenting earthenware is far larger than it might be supposed. In the year 1869 gold to the value of £60,000 was used for this purpose in England alone, chiefly in the Staffordshire potteries.

For melting gold and silver alloys the furnace of Booth is preferred (Figs. 188 and 189), as every loss of the precious metal is avoided. The melting furnace is enclosed with iron plates and provided with an iron ash-pit, *A*. In order to recover any gold and silver which may adhere to the furnace-bars, *R*, these are occasionally melted and kept for a long time in a liquid condition, so that gold or silver may subside to the bottom.

Fig. 188.

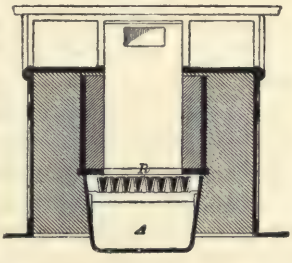
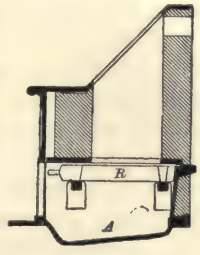


Fig. 189.



All alloys of gold, when polished, display colours differing from that of pure gold; they appear reddish or pale yellow. In order to give to such alloys the intense yellowness of pure gold they are boiled in a liquid (gold-colour) consisting of common salt, saltpetre, and hydrochloric acid. The action of the "gold-colour" depends on its property of dissolving—by means of the chlorine evolved—a little gold from the surface of the object, and then re-depositing it as a thin film, so that the surface may be richer in gold than the interior of the metal. The same object can be as well effected by the galvanic gilding process.

Gold Proof.—In order to ascertain rapidly the fineness of a gold alloy, goldsmiths make use of the touch-stone and the "touch needles." These are needles of gold alloyed with different proportions of silver or copper. A mark is first made upon

* It is also soluble, according to Mitscherlich, in selenic acid, and according to Gay-Lussac, in iodic acid. See also *Notes on the Treatment of Gold Ores*, by Fl. O'Driscoll, Assoc. M. Inst. C.E.

the stone with the article in question, which is then compared with marks made with the different needles. The mark is then treated with dilute aqua regia, and the quality is judged by the permanence, or the more or less rapid disappearance of the streak. This process, of course, can merely give approximate results, and it must be considered that the surface, especially of articles of jewellery, has in many cases been made richer in gold by the processes above-mentioned.

The best proof is cupellation. For this purpose the auriferous granule is melted up, according to its colour, with a triple, double, or equal weight of silver, and with about ten times the quantity of lead. It is then assayed in the usual manner. The argentiferous bead is flattened out, digested in nitric acid, the residual gold is washed, dried, and weighed.

Gilding.—Gilding is effected either by gold-leaf, by plating in the wet way, by fire gilding, or by the galvanic process.

Articles of wood, stone, cast-iron, &c., are gilt with leaf-gold. The gold leaf intended for this process is obtained by casting fine gold in ingots, forging it out in plates, and then rolling it into sheets. Twenty ducats yield sheet gold of 16 metres in length and 3 centimetres in width, which are cut up into quarters (so-called) of 3 centimetres in length. These sheets are first beaten out between leaves of parchment, and then between the exterior membrane of the cæcum of the ox. The finished leaves are laid in small books of very smooth paper rubbed with a little bole or ruddle to prevent the gold leaves from adhering. The residues serve for preparing (genuine) gold bronze. The objects to be gilt are first coated with a mixture of white lead and varnish or glue and chalk, and then covered with gold leaf. Articles of iron and steel, such as the blades of swords and the barrels of guns are first treated with nitric acid, heated until they turn blue, and then covered with leaf gold.

Talmi gold (first introduced into commerce by the Parisian manufacturer Tallois), is a yellow alloy of copper, coated with gold in the state of wire and sheets, and then further wrought up.

Gilding in the cold way is effected by dissolving fine gold in aqua regia, dipping linen rags in the solution, drying and burning them to tinder. The ash contains finely divided gold and carbon which are rubbed by means of a cork dipped in salt water upon the surface of the copper, brass, or silver to be gilt, and which must previously have been cleansed and polished.

Gilding in the wet way is conducted by plunging the objects into a dilute solution of gold chloride, or into a boiling mixture of dilute solution of gold chloride with a solution of sodium carbonate. Iron and steel which are to be gilt in this way are first coated with copper by immersion in a solution of copper sulphate. Articles of iron which are to be gilt in the wet way, may first be corroded with nitric acid, brushed over with a solution of gold chloride in ether, and heated. The action is almost instantaneous. A solution of gold chloride in sodium pyrophosphate has been recommended as a bath for gilding in the wet way.

Gilding in the fire, especially for articles of bronze, brass, or silver, corresponds very closely with silvering in the fire. The surface to be gilt is coated with a gold amalgam, with the intervention of a solution of mercury in nitric acid, and the article is then heated to expel the mercury, leaving the gold as a thin film adhering to its surface. The gold amalgam used consists of two parts gold and one part mercury. The gilding is either made brilliant by polishing or it is kept dead. If the gilding is to have the reddish polish of gold alloyed with copper, the bronzes, after the expulsion of the mercury, are dipped in melted gilders' wax (a mixture of wax, bole, verdigris, and alum), and the wax is allowed to burn off over a charcoal fire. The copper oxide of the verdigris is reduced to copper which combines with the gold to form a reddish alloy. Iron and steel are previously coated with copper.

Galvanic Gilding.—For preparing a gold bath 100 grammes of potassium cyanide are dissolved in 1 litre of distilled water. For this solution 7 grammes of fine gold are dissolved in aqua regia, cautiously evaporated to dryness, the residue taken up in a little distilled water, and the liquid added to the solution of the cyanide.

PLATINUM.

Occurrence.—Platinum is found only native and in small quantity in the so-called platinum-ore met with in Columbia and Peru, in alluvial deposits, and on the Ural, in the form of small, rounded, steel-grey grains—rarely nuggets—of a metallic lustre. Recently it has been found among gold-sand in California, in Oregon, Brazil, Haiti, Australia, and Borneo, and very lately in the Norwegian parish of Roeraas, disseminated in rocks, as also in the sands of the Ivalo River in northern Lapland.*

It was first discovered by the Spanish mathematician, Antonio d' Ulloa, in the gold-bearing sand of the river Pinto in Choco (New Granada); it was at first taken for silver, until in 1752 its distinct metallic character was recognised by Schaffer, the Master of the Swedish Mint.

The ores occurring in commerce under the names of platinum ore, native platinum, or crude platinum, are mixtures of platinum with palladium, rhodium, iridium, osmium, ruthenium, iron, copper and lead, and contain also generally grains of osmium-iridium, gold, chrome-iron, titaniferous iron, spinel, zircon, and quartz.

Platinum ores from Ural (I.), Columbia (II.), Choco (III.), Borneo (IV.), and California (V.), contained:

	I.	II.	III.	IV.	V.
Platinum	86·50	84·30	86·16	71·87	57·75
Rhodium	1·15	3·46	2·16	—	2·45
Iridium	—	1·46	1·09	7·92	3·10
Palladium	1·10	1·06	0·35	1·28	0·25
Osmium-iridium	1·14	—	1·91	8·43	27·65
Osmium	—	1·03	0·97	0·48	0·
Copper	0·45	0·74	0·40	0·43	0·20
Iron	8·32	5·31	8·03		
Lime	—	0·12	—	8·40	7·70
Quartz	—	0·60	—		

The yearly supply of platinum is about 450 kilos. from the South American localities, 120 from Borneo, and 3600 from the Ural.

For the extraction of platinum from its ores they are first heated to redness and covered with cold aqua regia to remove gold; filtered, and the residue is again treated with aqua regia in a retort. The liquid distilled off contains osmium, whilst the undissolved residue consists of osmium-iridium, ruthenium, chrome-iron and titaniferous iron, whilst the solution contains palladium, platinum, rhodium, and a little iridium. The solution is neutralised with sodium carbonate and mixed with a solution of potassium cyanide, when the palladium is eliminated as a cyanide. The filtrate is concentrated by evaporation, and mixed with a saturated solution of ammonium chloride whereby $PtCl_4 2NH_4Cl$ is thrown down along with a small quantity of iridium. For technical uses the slight admixture of iridium is advantageous, as it confers upon the platinum the hardness necessary for working. The double ammonium-platinum chloride is dried and ignited leaving metallic platinum as a spongy mass (platinum sponge). This mass is then compressed in iron cylinders with steel pistons at a red heat, repeating this operation until the metal has the appearance of melted platinum, and is sufficiently dense for working.

According to Descotils, the platinum ores are to be smelted with 2 to 4 parts of

* It is very probable that platinum may have often been overlooked in California and Australia in the earlier and pre-scientific days of gold-digging.

zinc, the homogeneous brittle mass powdered and sifted, the zinc and the chief part of the iron dissolved out with dilute sulphuric acid, and the residue treated first with nitric acid to extract iron, copper, and lead, and then with aqua regia, which dissolves the platinum, &c., much more easily on account of its finely divided state. The process is then completed in the usual manner.

In the process of H. Sainte Claire Deville and Debray lead is used to dissolve all the metals of the platinum ore except osmium-iridium and iron. The ore is smelted in a reverberatory with an equal weight of galena and a little glass, yielding a regulus, at the bottom of which is the osmium-iridium, whilst a lead-slag floats on the surface of the regulus. This platiniferous regulus is refined on the hearth, when all the foreign metals are volatilised and absorbed into the hearth, whilst the platinum which remains is refined in lime crucibles. The lime here acts upon all such impurities as silicon, iron, copper, &c., and converts them into fusible compounds, which withdraw into the porous mass of the crucible. To fuse 1 kilo. of platinum there are required 100 litres oxygen and 300 litres of coal-gas. Still higher temperatures may be obtained with the electric smelting furnace of W. Siemens which, however, has not yet been applied for this purpose.

Properties.—Platinum is almost of a silvery-white but with a slight steel-grey cast, it is shining, malleable, and ductile and so soft that it may be cut with shears. It may be drawn out to wire which is almost microscopic. For this purpose a platinum wire is coated with silver and drawn as finely as possible in the ordinary manner. It is then treated with nitric acid, which dissolves off the silver and leaves the platinum untouched. Its sp. gr. is 21·504. It can be welded and fused before the oxyhydrogen blast. Platinum sponge and platinum black have the property of condensing gases in their pores in extraordinary quantities. If hydrogen comes in contact with these substances it combines with oxygen so as to form water by intervention of the platinum. This combination is effected with so great a development of heat that the platinum is ignited and hydrogen passed up against it takes fire. (Döbereiner's hydrogen lamp.)

Platinum black is platinum in a state of very fine division; it is produced either by boiling platinum sulphate with sodium carbonate and sugar, when the platinum black is precipitated as a powder, or by melting together platinum and zinc, and dissolving the alloy in dilute sulphuric acid. Platinum black possesses the property of condensing gases in a still higher degree than spongy platinum, and serves thus for converting alcohol into acetic acid.

Platinum may be worked up either by rolling or by fusion and casting. The manufacture has been lately developed by Heraeus, of Hanau, and especially by Matthey, of the firm of Johnson & Matthey, of London. It serves for chemical and technical apparatus, which are not attacked by high temperatures or by most substances. Still they must be treated with great care, and especially must not be exposed to contact with fused caustic alkalies, melting saltpetre, free chlorine, aqua regia, sulphur and sulphides, phosphorus, melted metals and easily reducible metallic oxides (especially along with carbonaceous matter). The articles made of platinum are sheets, wires, crucibles, spoons, nozzles for blow-pipes, points for lightning conductors, retorts, forceps, pans for refineries and sulphuric acid works; it serves also in the manufacture of galvanic elements, glow-lamps, and for coating copper capsules, porcelain, stone-ware and glass. Platinum has been used for producing the standard measures (copies of the original Paris metre) resolved on by the International Commission of Weights and Measures. The standard measures, which were prepared by Mr. Matthey (Johnson & Matthey), consist of an alloy of 90 parts platinum and 10 parts iridium, and are much harder than pure platinum. Similar alloys are now preferred as the material for platinum crucibles.

In Russia, platinum was coined, from the year 1828, into 3, 6 and 12 rouble pieces. In 1845, the coining of these pieces (which had already consumed or wasted 14,250 kilos. of this indispensable metal) ceased, and the pieces already issued were called in.

In 1877, S. Kern found in the metal of platinum crucibles, made in Paris—

Platinum	.	98·70 per cent.	...	97·90 per cent.	
Iridium	.	0·56 „	...	1·40	„
Iron	.	0·30 „	...	—	
Copper	.	0·22 „	...	0·67	„

TIN.

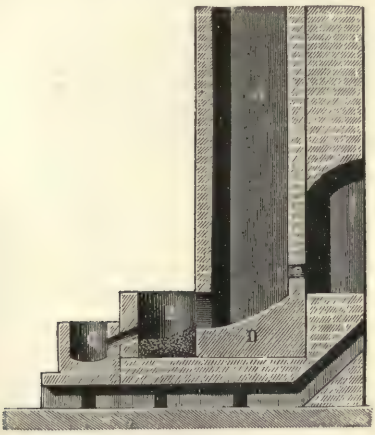
Tin is one of the rarer metals. It never occurs native, but oxidised as cassiterite or tin-stone, SnO_2 or as stannine, tin sulphide, combined with other sulphides in tin pyrites $(2Cu_2S + SnS_2 + 2FeS,ZnS)SnS_2$.

Tin-stone is found *in situ* in granite, syenite, mica-slate, porphyry, &c., or in secondary and alluvial deposits (wash-tin, tin sand, &c.); contains in addition to tin-oxide, sulphur, arsenic, zinc, iron, copper, and other metals. It also occurs in the sand of rivers as almost chemically pure stannic acid. Such tin, and that obtained from washings, gives a much purer metal than vein-tin, as Nature has here already executed a mechanical purification. The vein ores are first separated by stamping and elutriation from the gangue and freed from sulphur, arsenic, and antimony by roasting.

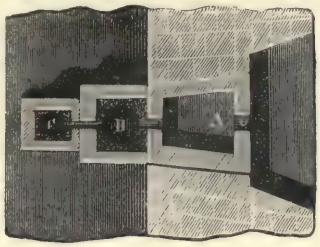
According to the process in use at Altenberg in the Erzgebirge, the ore, after roasting, is smelted in shaft-furnaces, 3 metres in height (Fig. 190, I. and II.). The

Fig. 190.

I.



II.



walls, constructed of granite, rest upon a foundation of gneiss. The bottom stone, D, consists of one piece, hollowed out to form a dish. The fore-hearth, B, is connected by a tap-hole with an iron pan; the tuyère of the blast opens into the shaft at *o*. The ore mixed with coal, coke or charcoal, is placed in the shaft, A; the reduced tin collects in the fore-hearth, B, whence it flows into the pan, C. It contains iron and arsenic; from these impurities it is freed by eliquation on a hearth covered with ignited fuel. The pure tin melts first, flows through the fuel and collects on the tapping hearth, whilst a less fusible alloy of tin with iron, &c., remains in grains, which the Saxon miners call "thorns." The slags, which often contain 15 to 18 per cent. of tin, are smelted from time to time, yielding tin and a residue which, like the "thorns," consists of an alloy of tin and iron.

The tin obtained in shaft furnaces is very pure, containing scarcely $\frac{1}{10}$ per cent. of foreign metals. It is known as grain tin. The less fusible alloy is re-melted and sold as block tin. The presence of tungsten in the ores greatly interferes with the production of pure tin.

Australia produces yearly 10 to 15,000 tons, Britain 10,000, the Straits (Malacca) 10,000, Banka and Billiton 9000, Tasmania 3–5000, Altenberg 150.*

* It is found in New Granada, but the Western hemisphere contributes practically nothing to the commercial supply. Tin ores have also been worked in Central Asia, on the north and north-west of Afghanistan, but nothing definite is known concerning the extent and the capabilities of the deposits.

Tin has a silvery colour, but with a bluish cast, and a perfect metallic lustre. Next to lead it is the softest of the metals, but it possesses so much hardness that a bar of tin, freely suspended, gives a sound if struck. If bent it creaks, the more decidedly the higher its purity. Tin is very malleable, and can be wrought out to very thin leaves. If rubbed it imparts a peculiar and very persistent smell to the hands. The sp. gr. of pure tin is 7·28, but by hammering and rolling it can be raised to 7·29.* If heated almost to its melting-point, it becomes brittle, and can be broken up with the hammer. If used for castings, its lustre and tenacity depend entirely upon its temperature at the moment of casting. If heated so strongly as to show in flowing colours upon its surface, it appears striped after solidifying, and is called "red shoot." If heated too little it is called "cold shoot", and has a dull surface. At a strong white heat tin begins to boil and slowly evaporates. Melted tin becomes covered on its surface with a grey film, consisting of stannous oxide and metallic tin. By continued fusion in presence of air, tin is completely converted into a yellowish-white oxide, tin-ashes. On exposure to the air tin gradually loses its lustre.

Assay of Tin Ores.—For suitable methods we may refer the reader to "Select Methods in Chemical Analysis," by W. Crookes, F.R.S., p. 403 ; for the determination of lead in samples of tin, *ibid.* p. 409; for the separation of tin from copper, *ibid.* p. 410 ; and for the commercial analysis of tinware, *ibid.* p. 413.

Uses.—Tin is used in alloys (gun-metal, bronze, phosphor-bronze, bell-metal), and formerly more than at present for domestic and table requisites, for the capitals of stills, for cooling-apparatus, and tubs, dye-pans, and laboratory appliances. Tin is used along with lead, because these alloys are harder than either of the constituents alone, and resist wear better. By rolling and beating, tin is extended to tin-foil, the stronger sort of which is used for lining mirrors—so-called silvering—and the thinner kind for lining boxes, wrapping up chocolate, fancy soaps, sweetmeats, &c.† Stölzel found in four qualities :

Tin	97·60	97·81	98·47	96·21
Copper	2·16	1·23	0·38	0·95
Lead	0·04	0·76	0·84	2·41
Iron	0·11	0·10	0·12	0·09
Bismuth	trace	—	—	—
Nickel	—	—	—	0·29
	99·91	99·90	99·81	99·95

False leaf silver is tin mixed with a little zinc, and beaten out to thin leaves. Tin with small proportions of copper, antimony and bismuth, is often used for spoons, &c. A similar alloy is Britannia-metal, used for spoons, candlesticks, coffee- and tea-pots, as it approximates more to silver in its appearance than does tin ; it is harder, takes a better polish, and is more easily wrought and rolled out to sheets. It consists of 90 parts of tin, with 10 of antimony, and generally small quantities of copper (0·09 to 0·8 per cent.); frequently 1 to 3 per cent. of zinc; in one case, in an English sample 1·83 per cent. of arsenic. Britannia-metal articles are sometimes silvered.

As the metals with which tin is likely to be contaminated—accidentally or intentionally—have all a higher sp. gr. than tin, a determination of the sp. gr. of a sample gives an indication of its purity. Alloys of tin and lead in the ordinary proportions have the following specific gravities :—

	Sp. gr.		Sp. gr.
1Sn + 1Pb	8·864	1Sn + 4Pb	10·183
1Sn + 2Pb	9·953	2Sn + 1Pb	8·226
1Sn + 3Pb	9·9387	3Sn + 1Pb	7·994

* Solid pieces of pure tin float upon a bath of melted tin, just as does ice upon water.

† There occur in commerce, however, tin-foils containing a large percentage of lead, and consequently unfit for contact with articles of food.

Tin-ash, mentioned above, is used in polishing glass and metals, and for giving a white colour to enamels.

Tinning.—The objects to be tinned are previously cleaned by scouring, washing, or by acid liquids. The oxidation of the layer of tin to be applied is prevented by means of resin and sal-ammoniac, which reduce immediately any oxide that has been formed. Copper and wrought-iron are easily tinned, the vessel or other article to be tinned being heated almost up to the melting-point of tin; melted tin is then poured upon it, and the metal is spread over the surface of the copper, &c., by means of a bunch of tow, upon which sal-ammoniac has been scattered. Articles of brass, *e.g.*, pins, are boiled in tinned pans with granulated tin, and with a solution of potassium bitartrate. The tinned articles are then rubbed with bran or sawdust. Sheet-iron, which must be of the best quality, before tinning is very carefully cleansed with bran-water which has turned sour, and with dilute sulphuric acid, plunged into melting tallow, and then into melted tin. The tallow protects the tin from oxidation. After the sheets are sufficiently coated with tin, they are taken out, cleared from any excess of tin, and cleaned with bran.*

The clippings of tin-plate (tinners' waste), which contain 7 to 8 per cent. of tin, are collected, freed from tin, and used as scrap-iron or worked up to ferrous sulphate. The removal of the tin is sometimes effected by treatment with a mixture of nitric and hydrochloric acids, and from the nearly neutral solution (which, of course, contains iron chloride) the tin is thrown down by means of zinc. Or the tin waste is suspended as an oxide in dilute sulphuric acid, the tin is deposited upon copper sheets connected with the negative pole and may be taken off in plates.†

If tin-plates are corroded with acids, it often results that deposits of a nacreous lustre appear on the surface, due to the crystallisation of the tin on rapid cooling. On treatment with a mixture of 2 parts hydrochloric acid, 1 part nitric acid, and 3 parts of water, the crystalline places are made apparent, which appear duller or brighter according to the unequal reflection of the light. Crystalline surfaces may be produced by the prolonged action of melted palmitic acid. Such tin-plate is called *moiré metallique*. They are found with large regular hexagons, others with squares, the small crystals recalling the aspect of granite or gneiss; others like mosses and ferns, large trees or seaweeds, a strange regularity along with fantastic irregularity. Splendid effects may be produced with the aid of lacquers, showing the lustre of many-coloured nacre, along with the full colours of tortoise-shell, granite-like plates, apparently covered with elegant dendrites, the lustre of which is heightened by appropriate colours.

BISMUTH.

Bismuth ranks among the rarer metals. It is found at Schneeberg in the Erzgebirge, in Peru, Chile, and Australia; mostly native in cobalt and silver veins in granite, gneiss, mica-slate, and in transition formations. It is also met with oxidised as bismuth ochre, Bi_2O_3, and combined with sulphur as bismuthine, Bi_2S_3, or as cupreous bismuth (containing 49·24 per cent. of bismuth).

The chief supply of bismuth is from the Saxon blue-colour works at Oberschlema and Pfannenstiel, which are in possession of the great deposit of bismuth at Schneeberg. Formerly bismuth was obtained from its ores by eliquation, the mineral being heated in iron pipes, laid in a sloping position, when the bismuth was liquefied, and

* Tern-plates are sheet-iron coated, not with pure tin, but with an alloy of tin and lead. Tern is employed for inferior wares, but should never be used for tins or cans for preserved milk, meat, fruits, or vegetables, all of which act more or less upon the metals, and dissolve a quantity of lead, which may in time have serious effects. It has also been found that in soldering up canned provisions zinc chloride has been used instead of resin and with most serious effects.

† No process as yet known is perfectly satisfactory. Tern-waste is quite useless.

ran off. In this manner, only that part of the bismuth was obtained which was present in the metallic state, and even this very incompletely. The rest, on the smelting of the cobaltiferous residues, passed into the smalt-glass, when the bismuth collected in the cobalt-speiss, and was again separated by eliquation. This imperfect process has long ago been abandoned.

At the Saxon blue-colour works, all the bismuth and bismuth-cobaltic ores are first roasted, and are then smelted in the crucibles of the smalt-glass furnaces, with the addition of carbon, iron, and slag. The reduced metal beneath the slag forms two very distinct layers, the upper, consisting of cobalt-speiss (cobalt-nickel and iron-arsenides), the lower of bismuth. As the melting point of bismuth is very low, it is run off in a liquid state as soon as the superjacent layer of speiss has solidified.

This crude bismuth is tolerably pure, containing only small quantities of iron, cobalt, nickel, lead, silver, sulphur, and arsenic. The purification is effected by kindling a wood fire on an iron plate, slightly sloping, and allowing the blocks of crude bismuth to be slowly melted down. The refined bismuth, collected in an iron dish previously warmed, is ladled out into hemispherical iron moulds, which have at the bottom the arms of Saxony. These hemispheres weigh 10 to 12 kilos., and constitute the commercial article.

At Freiberg bismuth is also obtained, in the wet way, from the litharge and ash from silver refining. The ash is extracted with dilute hydrochloric acid. Basic bismuth chloride is precipitated from the solution by the addition of water, and is reduced by melting in iron crucibles with soda, charcoal, and glass.

The blue-colour works of Saxony produce yearly 18,000 kilos. of bismuth ; Freiberg, 2500 ; Johanngeorgenstadt, 1500 ; Altenberg, 500 ; and Britain (from exotic ores), 2500 kilos.

Properties.—Bismuth is a reddish-white metal, of a high lustre, a foliaceous texture, and so brittle that it may be pulverised. It is slighty malleable, if carefully hammered.

The respective composition of Saxon (I.), Peruvian (II.), and Australian (III.) bismuth is as follows :—

	I.		II.		III.
Bismuth . . .	99·77	...	93·372	...	94·103
Antimony . . .	—	...	4·570	...	2·621
Arsenic . . .	—	...	—	...	9·290
Copper . . .	0·08	...	2·058	...	1·944
Silver . . .	0·05	...	—	..	—
Sulphur . . .	0·01	...	—	...	0·430
	99·91	...	100·000	...	99·388

Uses.—Bismuth is used for alloys, melted as oxide, with boric and silicic acids, for optical glasses, and of late to a considerable extent for porcelain colours, and, as basic bismuth nitrate, for a cosmetic (*blanc de fard*); also for medicinal purposes. Among the chief alloys of bismuth are those with lead, tin, and cadmium. Newton's fusible metal consists of 8 parts bismuth, 3 tin, and 5 lead, and melts at 64·5°. Rose's metal consists of 2 bismuth, 1 lead, and 1 tin, and melts at 93·75°. A small addition of cadmium makes these alloys still more fusible. An alloy of 3 parts lead, 2 tin, and 5 bismuth, melts at 91·66°, and is suitable for obtaining clichés of woodcuts, printing formes, stereotypes, &c. A similar alloy serves for metallic baths used in tempering steel work, as also for pencils, used instead of graphite, upon paper prepared with bone-ash.

ANTIMONY.

Occurrence.—Antimony is found chiefly combined with sulphur, as stibine or antimony-glance, Sb_2S_3, in beds and veins in granite and in crystalline slate and tran-

sition formations. It is also met with as antimony oxide, Sb_2O_3, in the minerals valentinite (rhombic) and senarmontite (tesseral). The latter occurs in great quantity at Constantine (Algeria) and in Borneo.

Extraction.—Antimony is chiefly obtained by fusion followed by desulphurising. The smelting is effected in some districts, as at Wolsberg near Harzgerode, in crucibles, *b*, (Fig. 191). The bottoms are perforated and fixed upon smaller crucibles, *c*, which are surrounded with hot sand or ashes. At both sides of the crucibles there are draught-holes. In order the better to utilise the fuel, there is used in other places a similar arrangement with two melting pots or crucibles, which are set on the hearth of a reverberatory in such a manner that only the upper, charged crucibles are touched by the flame. The lower crucibles are set outside the furnace in front of larger crucibles in small vaults, and are connected with the furnaces by means of stone ware pipes (Figs. 192 and 193). The eliquation of antimony sulphide can be effected most rapidly when the ore—as is done at Ramée in La Vendée, is placed directly upon the sloping hearth of a reverberatory (Fig. 194) and care is taken that the antimony

Fig. 191.

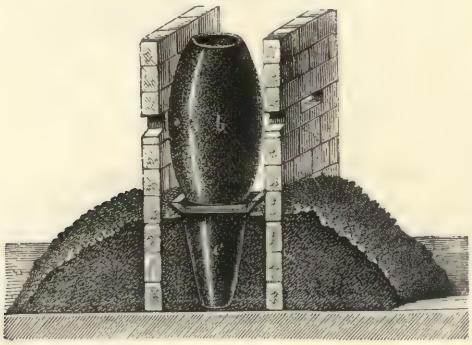


Fig. 192.

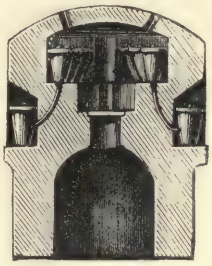


Fig. 193.

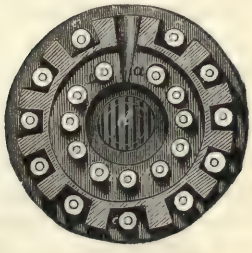
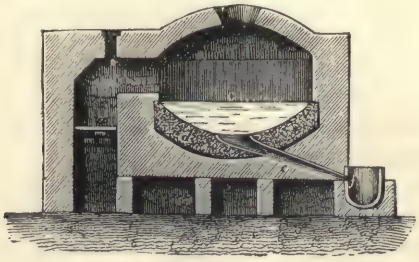


Fig. 194.



sulphide, as it melts out of the ores, flows from the lowest point of the hearth through the channel, *e*, to a receiver, *f*, placed outside the furnace.

After the ore is in a softened condition and a layer of slag has been formed, the tap-hole is opened and the heat is raised. The sulphide remaining in the ore collects beneath the slag and is let off after the end of the operation.

For obtaining antimony by the roasting process, the sulphide is spread on the sole of a reverberatory, and constantly turned over until it is chiefly converted into antimony antimoniate. The roasted product is reduced in crucibles. Heating alone would suffice for the reduction, as the roasted ore always contains undecomposed antimony sulphide: $3Sb_2O_4 + 2Sb_2S_3 = 10Sb + 6SO_2$. But as antimony oxide would volatilise without a cover, the roasted ore is mixed with crude argol, or charcoal and soda. The regulus is allowed to cool slowly beneath the layer of slag, so as to acquire that stellated crystalline surface which is preferred in trade.

It is convenient to remove the sulphur from antimony sulphide by a precipitant (iron, or spongy iron). But in the exclusive use of iron the result of the decomposition is unfavourable, the separation of the iron sulphide from antimony being difficult, on account of the approximate equality of their specific gravities. From this reason, and to render the sulphide at once specifically lighter and more fusible, an alkaline carbonate or sulphate is added. To 100 parts of antimony sulphide, 42 parts of iron waste (wrought), 10 calcined salt-cake, and 3·2 parts of charcoal are found suitable proportions. To obtain a regulus free from arsenic, 16 parts of the metal thus obtained (to which, if not sufficiently ferriferous, 2 parts of iron sulphide may be added) are melted with 1 part of antimony sulphide, and 2 parts of dry soda, and kept for an hour in fusion. The regulus is melted a second time with $1\frac{1}{2}$, and a third time with 1 part of soda, until the slag is of a light yellow. The presence of iron sulphide seems to be a condition for the elimination of arsenic, as a compound is formed similar to arsenical pyrites: $FeS_2 + FeAs_2$.

At Banya in Hungary antimony is smelted in the blast furnace.

An electrolytic extraction of antimony can be effected, according to Borchers, by decomposing a solution of 3·4 kilos. Sb_2S_3 and 7·2 kilos. $Na_2S.9H_2O$ corresponding to the formula $Sb_2S_3.3Na_2S$ with the addition of 2 or 3 per cent. sodium chloride. The resulting products were 2·435 kilos. antimony and in the solution 1·29 kilos. NaHS, 1·2 kilo. Na_2S_2 and 1·563 $Na_2S_2O_3.5H_2O$. The process at the kathode seems to have been according to the formula: $Sb_2S_3.3Na_2S + 3H_2 = Sb_2 + 6NaHS$, and that at the anode: $6NaHS + 3O = 3H_2O + 3Na_2S_2$.

Very poor antimony ores may be worked to advantage, as antimony tersulphide is easily soluble in very dilute solutions of sodium sulphide. To 1 mol. antimony tersulphide there must be present in the liquid 3 mol. sodium sulphide. After the former is dissolved, the liquid should mark 17° Tw. (if hot 12° to 14°). About 3 per cent. of sodium chloride, calculated on the entire quantity of the liquid, are added, which helps to separate the dissolved iron sulphide and lessens the resistance on electrolysis. If the solution remaining after the precipitation of the antimony is worked up for sodium thiosulphate, the common salt separates out again on the final evaporation. Iron vessels of any shape are used as decomposing cells and serve at the same time as kathodes. If a vessel of quadrangular section is used, the kathode surface may be increased by suspending in it iron plates. Between every two iron plates a lead plate, insulated from the iron, is suspended as an anode.

Properties.—The antimony of commerce contains arsenic, iron, copper, and sulphur. It is purified by melting with antimony oxide, the oxide oxidises the iron and the sulphur, and is reduced in the same proportion. Antimony is nearly of a silver white, with a yellowish cast; it has a strong metallic lustre and a foliaceous crystalline texture. Like its isomorphs arsenic and bismuth, it crystallises in distinct rhombohedrons. Its sp. gr. is 6·712 and its melting point 430°.

On solidifying, the melted metal does not expand. It is not extensible, very brittle, and can be easily pulverised. It exceeds copper in hardness. The powder sold under the name "iron black," and used for bronzing objects of plaster and papier maché, or of cast zinc (by which they obtain the appearance of polished steel), is finely divided antimony, obtained by precipitating a solution with zinc.

C. Himly found (1878) in three samples of commercial antimony:

Pb	0·34	0·34	0·73
S	0·23	0·12	0·11
As	0·09	0·36	0·09
Cu	0·01	0·02	0·02
Fe	0·35	0·34	0·16
Sb	98·98	98·81	98·87
	100·00	100·00	100·00

For the assay of antimony ores and regulus the reader is referred to *Mitchell's Manual of Practical Assaying*, 6th edit., edited by W. Crookes, F.R.S., pp. 556, 557, 558; also to *Select Methods in Chemical Analysis*, by W. Crookes, F.R.S., 2nd edit., pp. 396, 400, and 421.

Alloys.—An admixture of antimony in general renders metals more lustrous, hard, and brittle. "Hard lead" contains antimony up to 12 per cent. If, with Calvert and Johnson, we take the hardness of lead as 1, that of an alloy of 34·86 lead and 65·14 antimony = 11·7, and that of 86·50 lead and 13·50 antimony = 4. Thus, the hardness of lead may be increased almost twelve-fold by the addition of antimony. Alloys containing 17 to 20 per cent. of antimony form type-metal. Of the alloys of antimony and tin Britannia metal is the most valuable. It consists of 10 parts antimony and 90 parts tin. Similar alloys are pewter (89·3 tin, 7·1 antimony, 1·8 copper, and 1·8 bismuth); argentine (85.5 tin and 14·5 antimony), sometimes used for spoons and forks; and Ashbury metal (77·8 tin, 19·4 antimony, and 2·8 zinc), used for plummer blocks for locomotives and for the spindles of turners' lathes. An alloy of 5 antimony, 5 nickel, 2 bismuth, and 87·5 tin has been lately recommended.

The production of antimony is—

Britain	2000 tons.
France	580 „
Austria-Hungary	800 „
Germany	650 „
Italy	100 „
Spain	8 „

ARSENIC.

Arsenic occurs either native, or associated with metals, sulphur, and metallic sulphides. The oxides of arsenic never occur in nature is such quantity as to be of any technical importance. Small quantities of arsenic are found in all pyrites, and thus find their way into sulphuric acid.

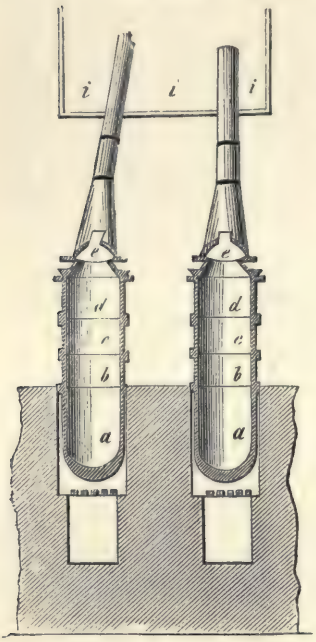
Production.—Arsenic is obtained by subliming native arsenic, or by heating arsenical pyrites (mispickel), FeSAs, and mohsine, Fe_4A_6, or by reducing white arsenic (arsenious acid): $As_2O_3 + 3C = 3CO + As_2$.

It is met with in commerce in greyish-black, crystalline crusts of a metallic lustre, and of sp. gr. 5·72. It evaporates at 180°, and melts (in closed vessels) at higher temperatures; and sometimes contains 8 to 10 per cent. of arsenic sulphide. Pure arsenic is used in the manufacture of shot, and for producing a light (by the combustion of arsenic in oxygen) used in trigonometric and military telegraphic signalling under the name of Bengal light.

Arsenious acid (arsenious anhydride, arsenteroxide, white arsenic) is obtained as a by-product in working up arseniferous cobalt, nickel, silver, and tin ores, in the blue colour works, in tin and silver furnaces, &c.; the arsenical ores being roasted in reverberatories and the vapours being led into flues and chambers in order to condense the arsenious acid. In Silesia arsenical pyrites are roasted expressly for the production of arsenious acid. The sublimation is effected in iron kettles (*a*, Fig. 195), upon which are set iron rings, *b*, *c*, *d*, and upon these again a dome, *e*, which is connected by means of pipes with the chamber, *i*. Along with this chamber there are other chambers. After all the joints and chinks have been luted up the sublimation begins. The heat must be increased so that the arsenious acid collecting in the chamber, *i*, begins to soften. When cold it appears as a perfect glass (arsenic glass) of a conchoidal fracture, vitreous lustre, and transparency, which in time becomes white, porcelain-like, and of an opaline or waxy lustre. Like the other preparations of arsenic, it is very poisonous. Sometimes there occur in arsenious acid small quantities of antimony sulphide and oxide.

Arsenious acid is used, dissolved in glycerine, as a mordant in calico printing; it serves also for purifying glass (especially crystal glass) during melting, for certain arsenical preparations (alkaline arsenites, Schweinfurt green, and other copper colours), as an antiseptic in stuffing the skins of animals [which is a dangerous blunder, as its antiseptic power is not great], for producing certain tar-colours; dissolved in hydrochloric acid for producing a grey colour on brass, and sometimes for hardening iron. One part of crystalline arsenious acid dissolves in 355 parts of water at 15°, whilst one part of the amorphous acid takes only 108 parts of water for solution.

Fig. 195.



Arsenic Acid, H_3AsO_4, is obtained by boiling arsenious acid in 4 parts of nitric acid of sp. gr. 1·35 and evaporating the solution to dryness, or by passing chlorine into arsenious acid suspended in water or dissolved in hydrochloric acid. It is sometimes used instead of tartaric acid in calico printing, and, besides, for preparing tar-colours, especially rosaniline or magenta.* Acid sodium arseniate (sodium dihydro-arseniate, NaH_2AsO_4), which is used in print works in the "dunging process," in place of cow-dung, is prepared by the cautious and prolonged heating of 36 parts arsenious acid with 30 parts sodium nitrate, or by heating a mixture of dry sodium nitrate and sodium arseniate. By saturating the solution of this salt there is obtained the so-called "saturated arseniate of soda" (disodium hydro-arseniate, $Na_2HAsO_4.12H_2O$), which is also used in dyeing and tissue printing.

Realgar, As_2S_2, is often found in crystals in mineral veins, or is produced artificially by melting sulphur with an excess of arsenic or arsenious acid, or, on the large scale, by submitting arsenical pyrites to distillation, or lastly—as formerly done in Freiberg—by melting the arsenic sulphide from the sulphuric acid works under increased pressure, and purifying the crude glass by sublimation. Realgar is a ruby-red mass of a conchoidal fracture, which, if mixed with saltpetre and ignited, burns, giving off a brilliant white light. The mixture for white fire consists of 24 parts saltpetre, 7 sulphur, and 2 realgar.

Orpiment, As_2S_3, is also found naturally, and is obtained artificially (as a mixture of As_2S_3 with arsenious acid) by melting together sulphur with arsenious acid or realgar, or by the distillation of a corresponding mixture of arsenical and sulphur pyrites. It forms massive, pale orange, transparent lumps (so-called yellow glass), which always contain arsenious acid up to 97 per cent., so that the yellow arsenic sulphide obtained in the dry way may perhaps be regarded as an arsenic oxysulphide. In the wet way it is obtained by precipitating a hydrochloric solution of arsenious acid by sulphuretted hydrogen, or by decomposing sodium sulpharseniate ($As_2S_3NaS_2$, obtained by fusing arsenious acid with sulphur and sodium carbonate) with dilute sulphuric acid, or lastly, by boiling a solution of arsenious acid in hydrochloric acid with sodium thiosulphate. In the last manner it is produced of an especially fine colour. Orpiment obtained in the wet way is used in oil-painting as a yellow pigment under the name of King's yellow. It was used in dyeing for the reduction of indigo, and it serves also, under the name of rusma, for the removal of superfluous hair. For

* Medlock process.

this purpose a mixture of 9 parts of lime and 1 part of orpiment is made up into a paste with water. Calcium hydrosulphate, prepared by passing sulphuretted hydrogen into cream of lime until it takes a greyish-blue colour, is now used in preference.

MERCURY.

Occurrence.—Mercury is found native, but chiefly as cinnabar, HgS, in beds and veins in crystalline slate rocks, in transition and Flötz formations, and is sometimes found in secondary deposits in loose, rounded fragments.

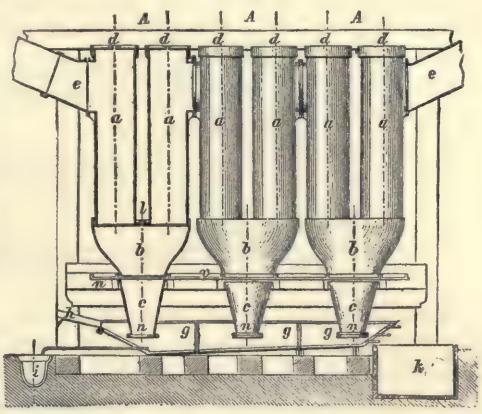
The chief localities are Almaden, or Almadingas, in Spain (Silurian), where it was raised in antiquity, and Idria, in Carniola (carboniferous). Cinnabar is also found in the Bavarian Palatinate near Wolfstein; on the Stahlberg, the Moschelandsberg, and the Potsberg, near Kusel; at Olpe, in Westphalia; in some parts of Carinthia, Eisenerz, in Styria; Horzowitz, in Bohemia; in several places in Hungary and Transylvania; at Dall' alta, in Venetia; on the Ural; in China and Japan; in the district of Sarawak, in Borneo; in Mexico; at Huancavelica, in Peru; and in large quantities in California, in transition formations.*

An impure cinnabar, mixed with earthy and bituminous matter, or a carboniferous shale, rich in cinnabar and paraffine, is known as mercury-lime-ore, and is peculiar to Carniola. A mercurial fahl-ore, containing from 2 to 15 per cent. of mercury, may also be mentioned.

Production.—At Idria the older shaft-furnaces are connected on both sides with a series of condensation chambers. The cinnabar is converted by the action of atmospheric oxygen into sulphurous acid and metallic mercury—

$$HgS + 2O = 2SO_2 + Hg.$$

Fig. 196.



At the works in Idria there was used in 1884 as fuel partly wood and partly lignite. In the previous year there were worked up 49,384·1 tons of ore, containing on an average 0·95 per cent. of mercury, besides 1044·2 tons of furnace residues produced on the spot, and containing on an average 10·12 per cent. of mercury, and rubbish from the foundations of old furnaces, 2968·3 tons, containing 0·51 per cent. of mercury. There were produced metallic mercury 4537·52 kilos., and intermediate products (stupps) 98·15 tons, containing 1053·2 kilos. of mercury, or a total yield of 5590·72 kilos. Hence the average proportion of mercury secured was 94·22 per cent.; if we omit the working up of the stupp and the mercury extracted from it, 94·06 per cent.; or a loss of metal, in round numbers, of 6 per cent.

The arrangement for condensing mercurial fumes introduced at Idria in 1882 consists of four ranks of pipes, which are formed of three condenser-elements, *A* (Fig. 196), each made up of two tubes, *a*, a twin-tube, *b*, and a cut-off portion, *c*, all fixed vertically upon the plates, *v*; the pipes, *a*, are closed with lids, *d*, provided with small openings for cleaning. The plate forms a part of the supporting surface for the tubes, *a*, formed by an internal circular rib of *b*, and has an aperture by which it is possible to get to the bottom of *g*, the box for receiving the stupp. The additional

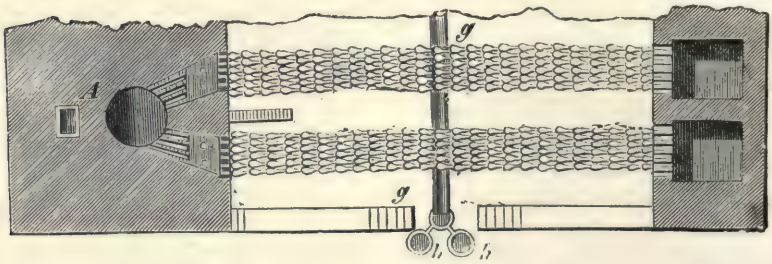
* An extensive deposit of mercury is said to exist in the Transvaal, but no particulars are as yet known.

pieces of pipe, *h*, effect the communication between the pipes which bring and which carry off the furnace-gases. All the cast-iron pipes, excepting *c*, and the boxes for collecting the stupp, are lined with layers of cement-mortar 10 to 15 millimetres in thickness, which has proved to be an excellent protection against the action of acid vapours. The gases enter the condenser at *e*, descend in the pipe, *a*, turn into the pipe, *a*, and rise in the second pipe, *a*, in order to traverse a similar course twice in the following portions of the condenser. The products of condensation are a mixture of finely divided mercury, particles of unburnt fuel, undecomposed hydrocarbons, ore, and ashes, as also moisture from the ore, and the fuel. The condensed steam-water, containing fluctuating quantities of soluble mercurial salts, is led into the wooden chests, *k*, where also solid matter which has been swept over may be deposited, and then into large cemented sumps, where it is sprinkled, in order to precipitate the mercury from its salts, with a lye of sodium sulphide, and is then allowed to run off. The stupp collecting under the water upon the sloping bottom of the chest, *g*, is raked upon the plate, *h*, after the free mercury and the water have drained off into dishes or chests. The mercury collecting at the deepest part of the chest runs off into *i*. The refrigeration of the condenser is effected by water conveyed from above, and allowed to flow down in a thin, uniform layer over the entire surface of the pipes, *a* and *b*; it then collects in the water-tight cistern formed by the plate *w*, and escapes through a lateral channel to the drains.

Fig. 197.



Fig. 198.



At the Almaden works the mercurial vapours are condensed in aludels, pear-shaped vessels of earthenware, open at both ends, and fixed together so that, as shown in Fig. 197, the thinner end of one fits into the wider end of the other, forming long rows after the joints have been luted together with clay and ashes. The cylindrical shaft-furnace, *A* (Fig. 198), is divided into two compartments by a perforated vault. The fire is made in the lower compartment and the ores are placed in the upper. Large blocks of a sandstone containing cinnabar are placed at the bottom (containing so little mercury that they do not admit of mechanical concentration), and upon these are placed the rich ores. The vapours pass into twelve series of aludels. Each series is 20 to 22 metres long and comprises 44 aludels. Consequently, there are in each furnace 528 aludels. The series lie on an inclined plane. From the lowest aludel the condensed mercury flows through the channel, *g*, into the stone cisterns, *h*. The vapours not condensed in the aludels are received in chambers, where they are completely precipitated. The mercury mixed with soot is purified by allowing it to flow down a slightly inclined plane; the mercury flows fairly clean into a sump; the sooty dust is left behind and is distilled again.

The furnaces used in America for coarse-grained ores are very similar to those devised at Idria, in 1871, by A. Exeli; they are iron-clad shaft furnaces. The shaft, *A*,

(Figs. 199 and 200) with twelve view-holes, *s*, is 1·87 metre in diameter; the four upper metres of the height are cylindrical, whilst the following 2·3 metres have the form of a truncated cone. Beneath the three fire-boxes, *f*, at the side, are the exit apertures, *a*. The round part of the furnace is clad with iron, 5 millimetres in thickness, enclosing a

Fig. 199.

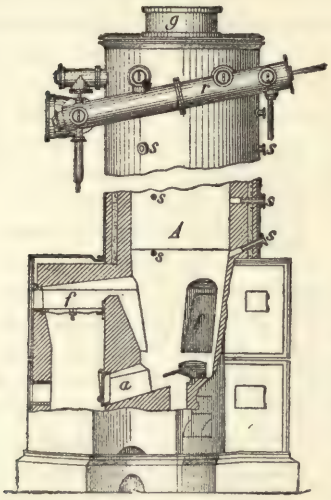
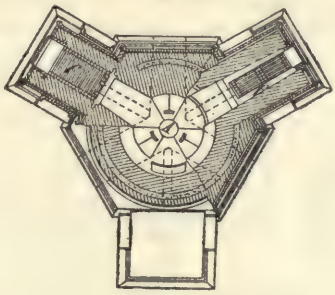
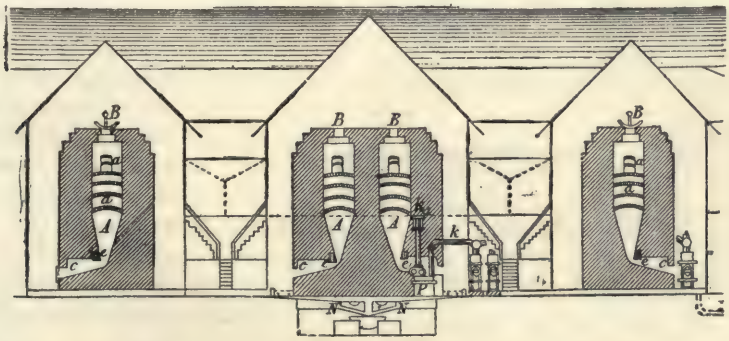


Fig. 200.



rough wall of ordinary bricks 0·12 metre thick, an inner wall 0·33 metre thick, which, as well as the filling between the two, is made of fire-proof stones. The angular part of the furnace is armed with cast-iron plates, well luted and screwed down; the cast-iron bottom plate slopes down towards the middle. The arrangement at the top of the furnace has a water joint, 0·6 metre; below the top are six apertures at equal intervals which convey the gases and vapours by means of the system of pipes, *r*; the gases and vapours escape into a large cast-iron main, and from thence to the condensers. In this system of pipes almost half the mercury collected is condensed. The furnace shaft is filled completely, but a space of 1·2 to 1·5 metre in height is left empty, where the vapours may collect. Every two hours at New-Almaden a fresh charge of 720 kilos. of rich ore and 1·5 per cent. of coke is introduced, so that 10 tons

Fig. 201.



are worked up daily with an expenditure of 2·7 cubic metres wood and the labour of two men for twelve hours.

The Knox-furnace (Figs. 201 to 203) first constructed at Knoxville, Redington, has been introduced at Sulfurbank, California, and Manhattan works, &c. The shaft-furnace, *A*, 11·7 metres high, and lined with fire-bricks, is constructed above and below of compact masonry, and is separated in its upper half by the five arches of masonry, *a*, of which the lowest project furthest outwards past the chambers, *d* and *d*, which are closed except one opening each (Fig. 203). The air-ducts, *e*, serve

to cool the masonry, which is 2·5 metres in thickness. The sole of the chambers, *d*, is protected against the penetration of the mercury by a strong iron plate. The charge of the furnace consists of two to three parts lumps (from 0·06 to 0·2 in size), and one part smalls; if the smalls are plentiful and moist the yield sinks to sixteen and even twelve tons daily. The shaft, which is closed at top with a bell-section, *B*, is charged with 55 tons of ore, and at the sloping mouth, *c*, one ton of dead ore is drawn out every hour, whilst fresh ore is added at *B*. Thus the charge remains in the furnace for three days. The grate, *d*, lies 6·1 metres below the top of the furnace; the fire is stirred up every half-hour. The combustion gases generated in the fire-box enter the ore through the openings between the arches, *a*, pass along with the products of distillation between the opposite arches into the space, *d*, and thence through the pipe, *k*, into the cast-iron condensers, *I*. These are rectangular chests with a sloping bottom 2·4 metres long, 0·74 metre wide, and 1·5 to 1·8 metre high, connected with each other by the pipes, *k*. The covering plates are turned up at the edges and kept cool with water, which runs over and trickles down the sides. The condensed products collect in the lowest parts of the bottom plate. The wooden condensers in connection are similarly arranged. The condensed products collect in the pans, *N*, from which the mercury is baled out into bottles. The acid water is run out into the recipients, *P*, in which a little mercury deposits. The vapours which issue from the furnace are very hot, so that the mercury condenses chiefly in the middle coolers. From the last condenser the gases, when quite cold, are driven by means of a Roots' blast, *Q* (four of which, along with the water-pump, *S*, a saw, &c., are driven by the engine, *R*), into the wooden channels, *U*, of 0·6 by 0·75 metre section. After running 89 metres each, two of them unite into a larger channe of 1·2 by 1·5 metre section, which conveys the gases for

Fig. 202.

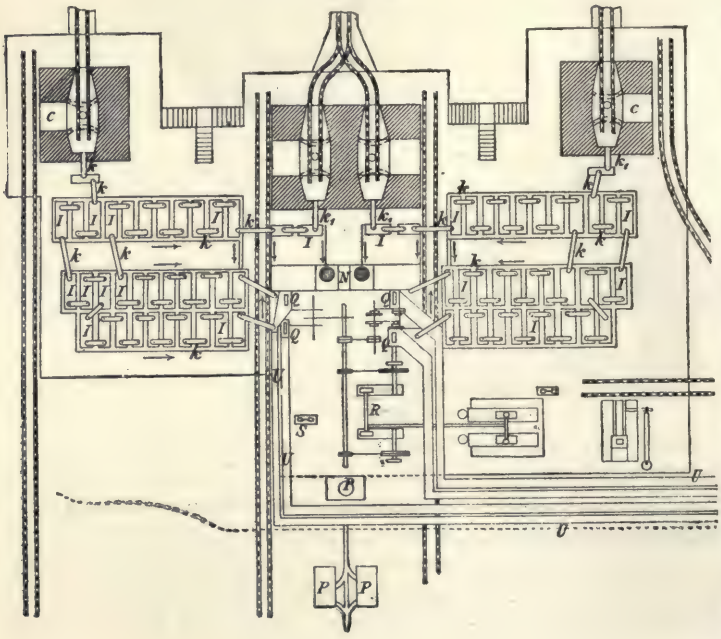
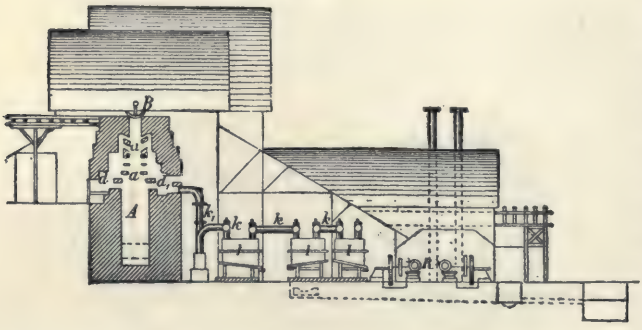


Fig. 203.

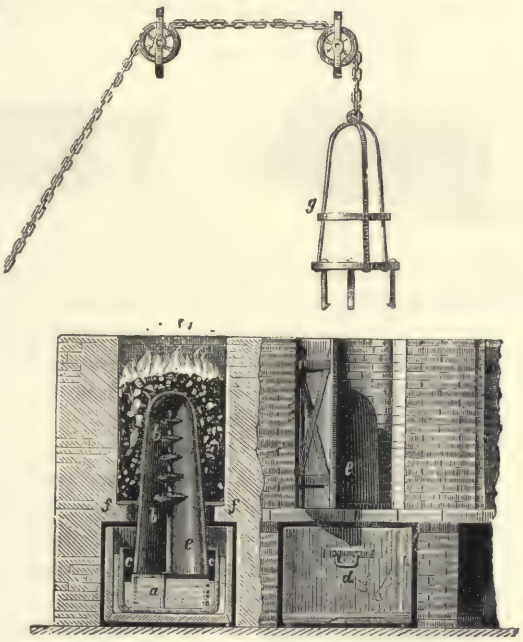


350 metres to a four-sided wooden scrubber tower, 4·5 metres high, filled with pebbles, over which water trickles. A furnace works up daily 96 tons of ore, and uses 36 cubic metres of firewood.

In 1883 California yielded 46,725 bottles of mercury, 28,700 from New Almaden. Between the years 1850-1883 California produced 1,357,403 bottles, each of 34·695 kilos. of mercury, Idria only 272,834, and Spain 1,044,139 bottles, each of 34·507 kilos. The price of mercury in 1874 reached a maximum of 12*s.* and fell in 1883 to a minimum of 3*s.*; in consequence, in March 1884, 22 of the 27 furnaces in California were out of work. In 1886 California yielded only 29,981 bottles.

At Horzowitz in Bohemia cinnabar containing clay iron ore is mixed with $\frac{1}{4}$ to $\frac{1}{3}$ its weight of forge scales and charged in a bell-furnace (Fig. 204) upon iron plates or dishes, *b b*, which are secured to an iron support and covered with an iron bell, *e*, dipping into water. The bell is placed in a furnace shaft of masonry and ignited by means of a coal fire. The mercury descending collects in *d*. Each bell, of which there are six in a furnace, contains 25 kilos. of ore and 12 kilos. of anvil scales; from 30 to 36 hours are required for the process.

Fig. 204.



The mines at Rosswalde near Stahlberg, in the Palatinate (opened in 1410), those at Landsberg, Potsberg, and Wolfstein contain cinnabar diffused through sandstone. The proportion of mercury is generally 0·005 and sometimes 0·01 per cent. To be worth extraction, it must form $\frac{1}{600}$ part of the ore. The decomposition of the cinnabar is conducted in iron retorts, of which 30 to 50 are placed in a galley-furnace. Lime is added to the ore when mercurial fumes are evolved, and there remains a mixture of calcium sulphide, thiosulphate, and sulphate.

The mercury works at Siele, near Castellazara, operate upon a very rich ore, partly in Hähner shaft-furnaces and partly in muffle-furnaces. The neighbouring works at Cornachino has two furnaces, each with three muffles of cast iron. Each is 2·7 metres long, 64 centimetres wide, and 32 centimetres in height. They are charged with 140 kilos. of ore and 84 kilos. of lime, both broken up and well mixed. This quantity is distilled off in six hours, so that the muffles are charged four times daily.

Details concerning the Chinese mercury mines are wanting. In 1782 a considerable quantity of mercury was exported from thence to South America.

Properties.—Mercury has a strong metallic lustre and a white colour, with a faint blueish cast. At common temperatures it is liquid; it solidifies and becomes malleable at $-35°.5$ and boils at 360°. Its sp. gr. is 13·5. It combines readily with lead, bismuth, zinc, tin, silver, and gold, forming amalgams; less readily with copper, and not at all, under ordinary circumstances, with iron, nickel, cobalt, and platinum. On these properties depend its applications for the separation of gold and silver from ores (amalgamation); amalgams are used for coating mirrors, for fire gilding, and for the friction-cushions of electrical machines.

Mercury is used in various scientific and technical apparatus, barometers, thermometers, levels, Sprengel pumps, &c. For directions for the detection of mercury in minerals, and for the assay of mercurial ores, see *Select Methods in Chemical Analysis*, by W. Crookes, F.R.S., pp. 292, 293, and 294.

ZINC.

Occurrence.—Zinc never occurs in the metallic state, but combined with sulphur as blende ZnS, and sometimes with small quantities of indium and gallium; it is found oxidised as calamine or zinc-spar, $ZnCO_3$, and as electro-calamine, zinc silicate, Zn_2SiO_4,H_2O. It is also found as willemite, an anhydrous zinc silicate, as red zinc ore, or zinc oxide, coloured reddish by oxides of iron and manganese (spartalite), as franklinite, Fe_2ZnO_4, as gahnite, Al_2ZnO_4 and in some fahl-ores.

The distillation of zinc from calamine and roasted blende in muffles is practised in Upper Silesia, at Stolberg near Aachen, in Westphalia, &c. The muffles are made upon moulds, and consist of fire clay and fragments of old muffles. The front side of a muffle has two openings; the lower is closed with a plate, *a* (Figs. 205 and 206), which is removed when the residues of the process have to be drawn out.

Fig. 205.

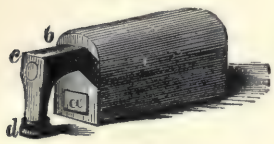


Fig. 206.



Above, a tube with an elbow joint is introduced, with an aperture which is closed at *c*, during distillation, and through which the charge is introduced. The liquid zinc flows out of *d* into the space below. The muffles are placed upon banks on the vaulted zinc furnace on both sides of a long fire grate, so that they are wrapped in the flame as much as possible. The zinc oxide formed at the beginning of the distillation contains nearly all the cadmium oxide, and serves for the preparation of cadmium. At the outset, the condensers are so cool that the vapours of zinc condense in them, not to a liquid, but to a solid, finely divided metal known as zinc powder. It contains about 98 per cent. of zinc, and is used as a powerful reducing agent, especially in calico printing. The zinc drops, afterwards formed in the old furnaces (drop zinc), are made to coalesce by remelting. In the recent furnaces the zinc is collected as a liquid in clay receivers and is taken out with iron ladles and poured into moulds.

Recently, gas-firing on the principle of Siemens or of Boetius has almost everywhere superseded grate-fires. In the latter case the furnace has two generators, *a* (Figs. 207 and 208), so that the fire-gases from each generator pass through half the furnace and then down in the middle through a common main shaft, or into the flues, *c*, placed between the muffles, and then through a channel connecting the latter into the main, *d*. The air required for gasification streams through the draught holes, *b*, into the furnace; the air for combustion is introduced through channels left in the walls of the furnace. The greater part of them are led through the furnace-walls in the reserved channels, *n*, in such a manner that this air meets the combustion gases, which have been half burnt in the combustion shaft, and so burns it gradually and completly, in order to produce a uniform heat. In order to convey away the vapours, which greatly annoy the workmen, the arch above the fore-cupels is provided with an exit slit, *s*, opening into the channel, *k*, leading into a small chimney.

On the Belgian system the distillation of the zinc is effected in stoneware pipes which lie in rows, over and alongside each other, slightly sloping. The pipes (Fig. 209) are cylindrical, generally 1 metre long, 18 centimetres in internal diameter, and closed at one end. The front opening of the pipes touches the front wall of the furnace and serves for introducing the charge, drawing off the zinc vapours, and removing the

residues. To each of these pipes there is attached a tube (Fig. 210), 25 centimetres in length, and to it again a tube of sheet iron (Fig. 211) 20 centimetres long, or a larger sheet iron receiver (coated within with clay), in which the zinc collects. Fig. 212 shows the section of a Belgian zinc furnace. The distilling tubes lie in ranks above each other, slightly inclining. For this purpose there are left steps in the back wall, *b d*,

Explanation of Terms.

Schnitt I-II. = Section I. II.

Fig. 207.

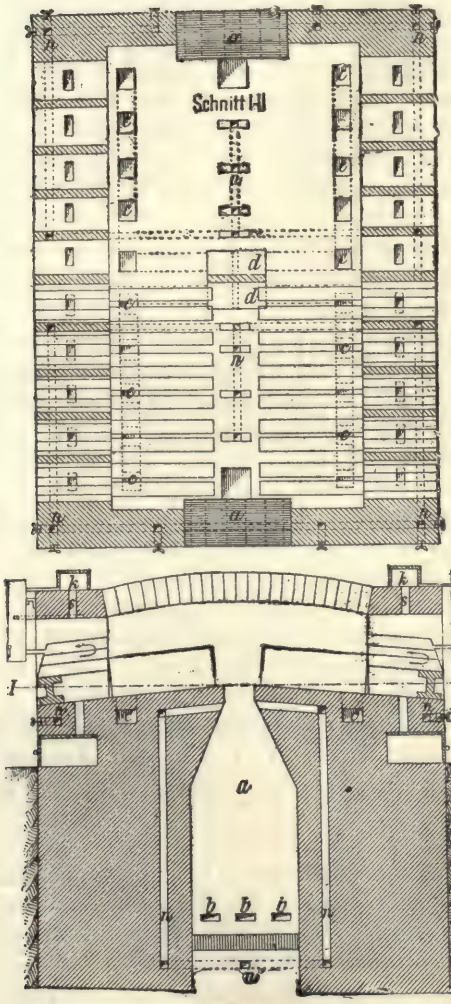


Fig. 208.

Fig. 209.



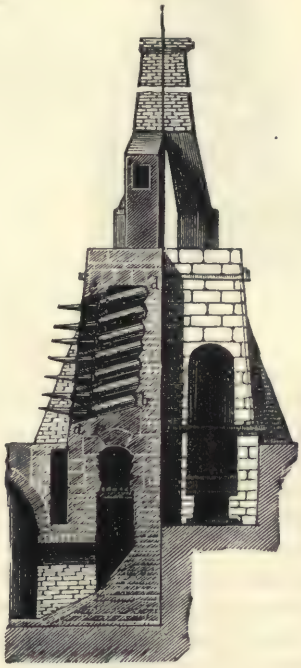
Fig. 210.



Fig. 211.



Fig. 212.



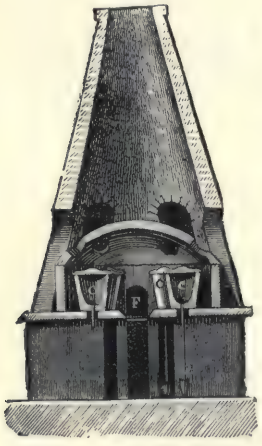
of the furnace, upon which the closed ends of the pipes rest. Whilst the Belgian furnaces formerly worked up daily 200 kilos. of ore in 30 tubes, those of recent make, with 70 tubes, use up 1200 kilos.

According to Liebig, the zinc works of the Märkisch-Westphalian Mining Union at Letmathe have in action twenty-six zinc furnaces, with seventy-six retorts each. Each furnace works up daily 1600 kilos. of ore ($\frac{2}{3}$ bleude and $\frac{1}{2}$ calamine), containing

on an average 45 per cent. of zinc, and produces 580 kilos. crude zinc. The consumption of fuel is about 23 hectolitres heating coal and 8 hectolitres reducing-coal. Three retorts are charged daily in each furnace.

The English method of obtaining zinc (Wales, Sheffield, Birmingham, Bristol) is the so-called downward distillation in crucibles. The reducing furnaces are so constructed that six to eight crucibles, *c* (Fig. 213), can be placed upon the hearth. The crucibles are made of fire-clay and are 1½ metre high. In the middle of the bottom is a hole through which the zinc fumes pass into the condensing tubes. The charge is introduced into the crucibles through a hole in the lid, which is left open for about two hours after charging, until a blue flame shows that reduction is beginning. The opening in the cover is then closed with a plate of fire-clay, the condensing pipe is joined to the opening in the bottom of the crucible, and below it is placed the receiver for the zinc, often filled with water, to prevent the zinc from spirting as it falls. The distilling zinc collects in drops and in fine powder mixed with zinc oxide, and is re-melted in iron vessels. The oxide which separates on the surface is skimmed off and the zinc is run into moulds. This process, especially at Swansea, has been latterly superseded by Belgian furnaces.

Fig. 213.



The production of zinc in blast furnaces has been attempted without success, as the zinc is re-oxidised to zinc oxide by the carbon dioxide.

From the receivers of the zinc distillation furnaces there escapes, as the author has shown, carbon monoxide nearly in a state of purity. This can be explained if the solid carbon forms only carbon monoxide—

$$ZnO + C = Zn + CO$$
$$-85{,}000 \quad +29{,}000 = -56{,}000 \text{ heat units,}$$

or if the carbon monoxide originally formed is reduced again ($CO_2 + C = 2CO$), so that the original process would be—

$$2ZnO + C = Zn_2 + CO_2$$
$$-170{,}000 \quad +97{,}000 = -73{,}000 \text{ heat units.}$$

The latter process takes up decidedly more heat than the former, and is therefore very improbable.

The reduction of zinc is hence effected chiefly or exclusively by solid carbon.

For the production of 65 kilos. of zinc there are required theoretically only 56,000 heat units, or 860 heat units per kilo., corresponding to 0·12 kilo. of coal. In practice twenty times the quantity of coal is required, so that the utilisation of heat is still very imperfect.

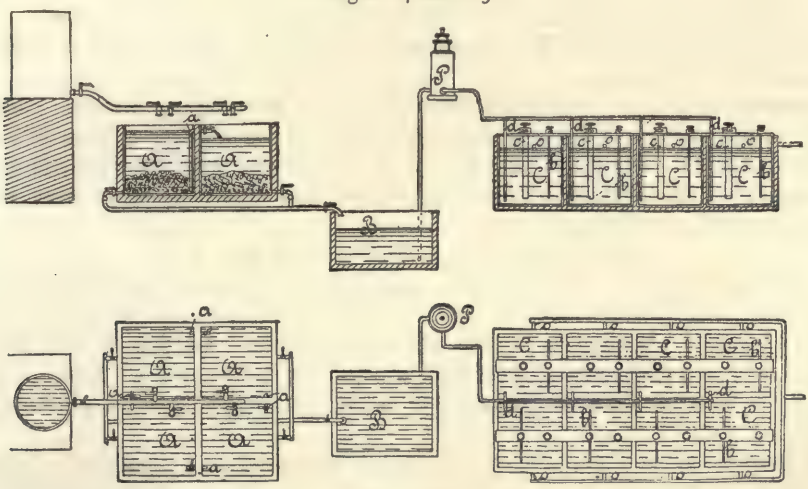
Production of Zinc by Electricity.—L. Létrange roasts blende at a low temperature to convert it into zinc sulphate. The roasted ores are lixiviated in walled tanks, coated with asphalte, *A* (Figs. 214 and 215), connected by pipes. The residues are worked up for lead and silver if present, the solution of zinc sulphate is collected in the cistern, *B*, and freed, if necessary, from iron, &c., and conveyed by the pumps, *P*, and the pipes, *d*, to the precipitating tank, *C*. The kathodes, *b*, consists of thin sheet zinc, but polished copper or brass may be used, from which the deposited zinc is easily removed. The anodes, *c*, are of carbon, platinum, or lead. The lye rendered acid by the elimination of the zinc flows away continuously through pipes, *o*, in order to be used for dissolving fresh masses containing zinc oxide. If very pure calamine or zinc-ash is to be worked up, it is mixed with carbon and suspended in the bath in a porous vessel as an anode.

Létrange fitted up such an installation for working up zinc-ash at his rolling mills at St. Denis; a second installation for blende containing lead and silver has been erected in the Department du Var. When a stratum of metallic zinc, 4 to 5 millimetres

in thickness has been deposited upon the brass sheets serving as negative poles, a workman takes out the sheets and removes with a knife the zinc plate, which strips off like a piece of leather. The metal thus obtained is re-melted. The process devised by Létrange of converting the ores into sulphates by treatment with sulphurous acid and precipitating them electrolytically would render it possible to utilise large quantities of poor calamines.

According to Kosmann, there are obtained at St. Denis, in regular work from roasted blende with 1 horse power, 8 kilos. of zinc every 12 hours; consequently, with 1·4 kilo. coal per hour and horse power, for 1 kilo. zinc, 2·1 kilos. coal; whilst in the zinc works of Upper Silesia, there are consumed for 1 kilo. zinc, 2 kilos. coal for reduction, and 9·8 kilos. for heating. These statements appear doubtful, the assertion that 0·67 kilo. of zinc is obtained hourly per horse power can only hold good in cases of soluble anodes. For insoluble anodes the separation of 65 kilos. of zinc from the solution requires 170,000 heat units, consequently per kilo. 2615 heat units. Or as 1 horse-power hourly $(75 + 60 + 60) : 428 = 631$ heat-units, there are required at least 4 horse-power, or 7 horse-power (equivalent to 10 kilos. of coal) if only 50 to 60 per cent. of the power of the machine is utilised. It must also be remembered that with feeble currents hydrogen is always evolved.

Figs. 214 and 215.



In a solution of zinc sulphate of specific gravity 1·38 this escape of gas ceases if about 0·5 gramme zinc are deposited per second on 1 square metre of polar surface (corresponding to 16 ampères). For 10 per cent. solutions a density of current of 20–30 ampères is required per square metre.

Kiliani treats calamine, &c., with a solution of ammonia holding ammonium carbonate in solution. The liquid is led into decomposition troughs, the zinc is deposited at the kathode and oxygen is evolved at the anode. The kathodes are of zinc or brass; the anodes of sheet iron. The lye as it flows off is conveyed back into the closed dissolving tanks.

If soluble anodes are used, much less work is required from the current. If when decomposing a solution of zinc sulphate the anode consists of pure zinc, there are used at the negative poles for each molecule of $ZnSO_4$ 106,090 heat-units chemical work; but at the anode, exactly the same quantity is again developed, so that the current has merely to undertake the mechanical work of conveying the ions from one pole to the other. This mechanical work is expressed in the tension, or the development of heat. Jahn has shown that notwithstanding the differences of the chemical work to be per-

formed by the current, the total loss of energy of the chain, *e.g.*, by the oxide, zinc sulphate, and copper sulphate is the same, as in the separation of 1 kilo. copper in which 1807 heat-units are evolved, and of 1 kilo. zinc, 977 heat-units, corresponding to :—

	Free heat.		Chem. work.		
$ZnSO_4$. .	63,210	+	106,090	=	169,306 heat-units.
$CuSO_4$. .	114,744	+	59,960	=	170,704 ,,

According to the process of Blas and Miest the bath for working up blende consists of zinc sulphate $ZnSO_4 + ZnS = Zn + S + ZnSO_4$. As much zinc as is deposited on the kathode is dissolved at the anode, whilst the corresponding quantity of sulphur is separated out and can be freed from the gangue found in the sediment. The blende does not require to be roasted and the sulphate is obtained free. Less work is required from the current than in former methods. Since, then, only the decomposition of the zinc sulphide is in question, as

$Zn \mid SO_4$	→	$Zn \mid S$
− 106,090		+ 106,090 − 41,326 = − 41,326 heat-units.

Hence, there is needed for 1 kilo. of zinc 41,326 : 65·5 = 63·1 heat units, whilst for decomposing zinc chloride and sulphate more than double the chemical work is required. Pure blende is a bad conductor; the ordinary kind containing iron is better.

Luckow suspends in the bath a mixture of blende and coke, packed in boxes, but hitherto with little success.

Siemens and Halske recommend their process for working up blende. There are formed in the electrolytic decomposition cells zinc and ferric sulphide, according to the equation: $Zn\,SO_4 + 2Fe\,SO_4 = Zn + Fe_2\,(SO_4)_3$. The ferric sulphate thus formed has the property of dissolving zinc from sulphuretted zinc ores which have been slightly roasted, according to the equation:

$$ZnS + Fe_2(SO_4)_3 = ZnSO_4 + 2FeSO_4 + S.$$

A comparison of this and the former equation shows that after lixiviating slightly roasted zinc sulphide ores with the oxidised electrolytic liquid, the proportion of zinc and iron becomes as great as it was before electrolysis. Indeed, in this zinc process the necessary difference of potential between the anode and the kathode of the electrolytic bath is about twice as great as in the copper process previously described.

Properties.—Zinc is of a grey-white, slightly bluish colour, generally of a foliaceous crystalline, but sometimes very finely foliated, texture, with a strong metallic lustre on its surface. Colour, texture, and lustre vary in different directions, according as the zinc is more or less contaminated with other metals. According to Bolley, zinc, cast near its melting point and cooled rapidly, has the sp. gr. 7·178; if slowly cooled, 7·145: that cast at a red heat, if cooled rapidly, 7,109; if cooled slowly 7·120. By hammering and rolling, the sp. gr. may be raised to 7·2, or even 7·3. Pure zinc is slightly extensile, even at common temperatures, and can be rolled out to thin sheets without cracking at the edges. This property is lost if it is even slightly contaminated with other metals, so that ordinary zinc breaks under the hammer. It distils in a vacuum at 184°. At about 500° it ignites in the air, and burns with a pale green luminous flame to zinc oxide (zinc white). When heated, zinc expands considerably, more than any other technical metal (from 0° to 100°) by $\frac{1}{340}$ in length; if hammered, $\frac{1}{322}$. When melted, zinc on solidifying contracts. In casting zinc, the iron moulds must be strongly heated, and the temperature of the melted zinc must not be raised too high, that the solidification may take place gradually and at the smallest possible difference of temperature. The expansibility of zinc reaches its maximum between 100° and 150°, and even if contaminated with other metals it can be extended at this temperature. Hence it is worked out to sheets with

hot rollers. Above 150° the flexibility of zinc decreases, and at 200° it is so brittle that it may beaten to powder. Zinc is oxidised by superheated steam:

$$H_2O + Zn = ZnO + H_2$$

a property which is used in separating lead from zinc. In moist air zinc becomes coated with a film of oxide, which protects the subjacent parts from further oxidation. On account of its ready oxidation by water and acids, it is unsuitable for milk-pails and culinary utensils. An addition of 0·5 per cent of lead makes zinc more flexible, and such small proportions are therefore commonly added to zinc intended for rolling. But for zinc which is to be used for brass, even 0·25 per cent. of lead is very injurious, as it seriously lessens the strength of the brass. A large proportion of iron renders zinc brittle. For eliminating arsenic, L'Hote melts zinc with 1 to 1½ per cent. of anhydrous magnesium chloride. Commercial zinc can be freed from the greater part of foreign metals by repeated fractional distillation, keeping apart the portion which passes over first, and leaving the residue unvolatised. Traces of gallium and indium are sometimes found in the zinc of commerce.

Zinc from the Georg Works of the Silesian Association (I.), the brand CH of the same company (II.), from Giesche's successors (III.), and of the Furnace Sagan (IV.), in 1885, contained, according to Schneider and Peterson, in 100 parts:

	I.	II.	III.	IV.
Pb	1·4483	1·7772	1·1921	0·633
Fe	0·0280	0·0280	0·0238	0·032
Cd	0·0245	—	—	0·054
Cu	0·0002	—	0·0002	trace
Ag	0·0017	trace	0·0007	trace
As	trace	—	—	—
Sb	—	trace	trace	—
Bi	—	—	trace	—
S	trace	0·0020	trace	trace

A method for determining the value of zinc powder, which is often contaminated with zinc oxide, is to be found in *Select Methods in Chemical Analysis*, by W. Crookes, F.R.S., 2nd edition, p. 121.

Uses.—Zinc is applied in sheets for roofing, for gutters and spouts, for plates and cylinders in galvanic batteries; in alloys (brass, bronze, false gold-leaf); for desilvering work-lead, for generating hydrogen gas along with sulphuric or hydrochloric acid, for preparing zinc sulphide, zinc white, &c. Zinc precipitates copper, silver, lead, &c., from their solutions. If zinc and iron are placed in contact, the latter metal is protected from oxidation. Zinc is much used for castings, in place of bronze, cast-iron, and even of wrought stone and wood.

From 1860 to 1884 the total production of zinc in Europe has increased from 97,896 to 257,767 tons. In 1884 America furnished 23,240 tons of zinc.

CADMIUM.

Cadmium almost constantly accompanies zinc in its ores, especially in the Silesian calamine, and to a less extent in blende.

In some of its properties cadmium is intermediate between tin and zinc; it is tin-white, very brilliant, malleable and ductile, and gradually loses its lustre on exposure to the air. It has the sp. gr. 8·6; it melts at 360°, boils at 860° (Deville and Troost), or according to Becquerel at 746·2°, and can be easily distilled. It is met with in trade in rods weighing from 60–90 grammes. Silesian calamine contains as much as 5 per cent.; calamine from Wiesloch more than 2 per cent.; blende from the Harz 0·35 to 0·79; that from Przibram 1.78 per cent., that from Eaton in North America 3.2 per cent. The cadmium of these ores is concentrated in the brownish smoke which appears at the

beginning of the distillation of zinc. This fume, consisting of metallic zinc, zinc carbonate and cadmium, serves as the crude material for the preparation of cadmium. It is reduced by means of wood charcoal in small cylindrical retorts of cast-iron provided with conical receivers of sheet-iron. The metal found in these receivers is sold in the shape of rods of the thickness of a finger. Cadmium may also be obtained from cadmiferous zinc in the wet way by treatment with dilute hydrochloric acid. The zinc dissolves in the acid, and the cadmium is precipitated so long as zinc is present in excess. The residue (which also contains any lead present) is concentrated as far as possible and the cadmium is finally separated by distillation.

Silesia produces yearly about 2000 kilos. of cadmium.

If alloyed with lead, tin and bismuth it forms Wood's metal. An alloy of 10 parts cadmium, 13·5 tin, 49·8 bismuth, and 26·7 lead melts at 70°. The only preparation of cadmium in use is the sulphide, CdS, a splendid and permanent yellow pigment (*Jaune brilliant*) used by artists. It serves also for giving a bright yellow colour to toilet soaps and for producing a blue colour in fireworks. It is best obtained by precipitating a solution of cadmium sulphate with sodium sulphide, washing, pressing and drying the precipitate.

For the detection of cadmium in ores and alloys and for its determination, the reader is referred to *Select Methods in Chemical Analysis*, by W. Crookes, F.R.S., 2nd edition, pp. 331–333.

POTASSIUM AND SODIUM.

The production of the alkali metals differs from that of zinc only by the greater care required to preserve the metal from contact with the oxygen of the atmosphere.

For the manufacture of sodium, sodium carbonate is ignited with carbon:

$$Na_2CO_3 + C_2 = Na_2 + 3CO$$
$$-273{,}000 \qquad +87{,}000 = -186{,}000 \text{ heat-units.}$$

The separation of one kilo. of sodium requires, therefore, 4050 heat-units, decidedly more than in the corresponding reduction of metallic zinc from its oxide. With potassium the case is similar:

$$K_2CO_3 + C_2 - Na_2 + 3CO$$
$$-281{,}000 \qquad +87{,}000 =$$
$$-144{,}000 \text{ heat units.}$$

Fig. 216.



For manufacturing sodium 30 kilos. of dry sodium carbonate, 13 kilos. charcoal and 5 kilos. chalk are intimately mixed and placed in iron tubes, A (Fig 216), 1·2 metre long and 0·15 metre in diameter. The front cover supports an iron escape-tube leading to the flat iron receiver, *v*. For protection against the destructive action of the fire the tube A is usually encased in a wider fire-clay pipe. On heating to whiteness there escapes first carbonic oxide, then sodium, which becomes liquefied in the receiver and falls into an iron vessel filled with mineral oil (free from oxygen).

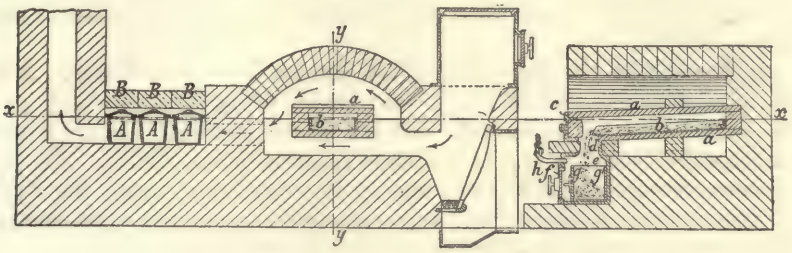
In this process there is obtained only about 40 per cent. of the theoretical yield, since a part of the sodium is burnt and a large part escapes reduction on account of the imperfect mixture.

Mactear gives the following estimate of cost for 1 kilo. sodium, 1887:—

Wear and tear of furnace, &c.	5·3	shillings
Loss of materials	2·7	,,
Labour	2·2	,,
Fuel	1·1	,,
	11·3	,,

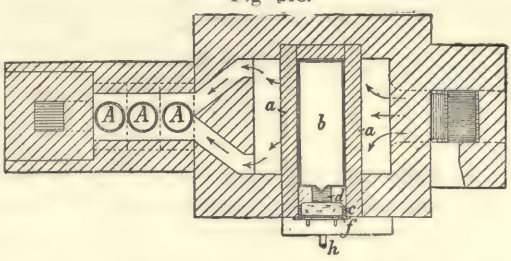
The recent proposal of Thompson, therefore, demands attention; 4 parts of dry sodium carbonate and 3 parts of tar are to be slowly heated to dull redness, the pulverised melt is placed in a box of sheet-iron *b* (Figs. 217 and 218), 10 centimetres in

Fig. 217.



depth, and provided with a spout. This is then placed in a fire-clay gas retort (previously heated to full redness) in such a manner that its spout is close to the lid of the retort *c*, which is then secured air-tight. Behind the lid the retort is freely connected by the aperture *e* with the chamber *g*, which can be closed air-tight by means of the door *f*. In the chamber a receiver *g* is placed, below the spout of the box *b*. From the chamber *g* a tube *h* passes outwards, and gives free escape to the carbon monoxide which is formed. The extinction of the flame of this gas shows the end of the process. The metal flows into the receiver. It is taken out as soon as the flame of carbonic oxide is extinct, and a fresh vessel is introduced. The box *b* is then removed and a freshly charged box is put in its place.

Fig 218.



Whilst the reduction is thus conducted the melt is prepared for further operations, the mixture of carbonate and tar being put in the iron pots *A*, through the apertures *B*, which can be closed with fireproof plates. These pots stand in the escape-flue for the combustion gases—which is enlarged at this point for the purpose—and thus the heat is utilised for preparing the melt.

Castner reduces sodium hydrate with so-called iron carbide, FeC_2, obtained by heating ferric oxide with tar. On heating 10 kilos. caustic soda and 2 kilos. carbide the decomposition is said to be effected as follows:

$$4NaOH + FeC_2 = Na_2CO_3 + Fe + 2H_2 + CO + Na_2.$$

The thermic relations would be:

	Heat-units.
For sodium hydrate $4 \times 102{,}000$ =	− 408,000
,, ,, carbonate . .	+ 273,000
,, carbon monoxide . .	+ 29,000
	−106,000 heat-units.

This would be decidedly more favourable than the old process; it must be con-

sidered that the heat liberated in the decomposition of FeC_2 comes in addition; its amount is not yet known.

According to Mactear, the mixture of sodium hydrate and iron carbide is placed in cast-steel crucibles in a furnace which is first gently heated for 30 minutes. The mass melts, and much hydrogen escapes in bubbles, whilst the carbide remains suspended in the melted soda. The crucible with its contents—now in tranquil flux—is lifted up and introduced into the heating-chamber of the main distillatory furnace. The cover of the crucible, which always remains in the furnace, has a convex border which fits into a groove in the edge of the crucible. From the lid a bent tube passes to the condensing apparatus, which has at its hinder end a small escape for the hydrogen evolved. It is also provided with a rod for preventing any obstruction from being formed in the tube during the distillation.

The gas given off at the beginning of the process is pure hydrogen. A sample drawn shortly before the end of the process contained 95 hydrogen and 5 carbon monoxide (which does not agree well with the above formula). A small excess of carbide induces the formation of a little sodium peroxide in the residue. The quantity of carbon monoxide formed is so little that it does not combine with the vapours of sodium. Hence, the formation of the black compound is prevented, which is otherwise apt to choke the exit-tube. The sodium obtained in this manner is pure.

After the completion of the process the contents of the crucible are poured out to make room for a new charge. The average composition of the residue is:

Sodium carbonate	77 per cent.
Sodium peroxide	2 „
Carbon	2 „
Iron	19 „

In preparing potassium less carbide is used to prevent the formation of carbon monoxide, and the distillation proceeds, it is said, smoothly.

The average weight of the residue of a mixture of 5·6 kilos. sodium carbonate and 1·97 kilos. carbide amounts to about 6 kilos. From this there are recovered 4·85 kilos. anhydrous sodium carbonate, corresponding to $3\frac{1}{2}$ kilos. sodium hydrate at 76 per cent.

If the manufacture is carried on as above laid down, the yield (according to Mactear) of 5·6 kilos. soda is 0·933 kilos. sodium.

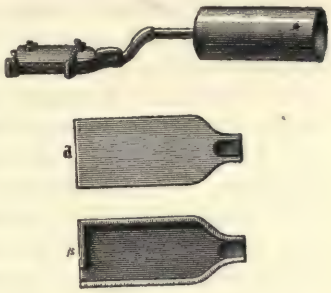
On each charge the distillation lasts $1\frac{1}{2}$ hour. Thus, as the furnace receives three crucibles it is possible to work up $3 \times 5{\cdot}6$ kilos. = 16·8 kilos. sodium hydrate, and to obtain 2·79 kilos. sodium and 14·5 kilos. sodium carbonate. The furnace yields daily from 268·7 kilos. sodium carbonate, 44·7 kilos. sodium, and 232·8 kilos. anhydrous soda.

The estimated daily working-cost for a furnace using the quantities of sodium hydrate and "carbide," is—

268·7 kilos. caustic soda	71	shillings
55·9 kilos. carbide	6	„
Labour	20	„
Fuel	17	„
Cost of converting 232·8 kilos. of sodium carbonate into hydrate	20	„
	134	„
Caustic soda recovered from 177·2 kilos.	46	„
44·7 kilos. sodium cost nett	88	„
1 kilo. sodium costs	2	„

As far as experience goes the wear and tear of the crucibles and the furnace is said to be unimportant, as 200 operations can be effected with the same apparatus, the loss for these items would be about 0·45 of a shilling on 1 kilo. sodium, or one-twelfth the amount in the old process. The statement of Mactear that a temperature of 830° is sufficient for the distillation can scarcely be accurate.*

Fig. 219.



Sodium is an important reducing agent in the preparation of aluminium, magnesium and silicon, as also as of various organic compounds.

The electrolytic production of sodium has not yet come into practical use. The oxygen compounds, as well as the chloride, the decomposition-heat of which = 98·000 heat-units (calories), are not suitable materials. Concerning sodium fluoride, a by-product in the production of aluminium, further experiments are wanting.

The production of potassium is hitherto effected according to the old process for sodium, but the oxygen must be still more carefully excluded. The potassium collects in the receiver (Fig. 219), consisting of the two parts, *d* and *s*. When this is almost full it is taken off, and plunged into mineral oil and purified by distillation.

The price of potassium is considerably higher than that of sodium, as there is formed during its preparation a black explosive compound of potassium and carbon, $K_6C_6O_6$, which diminishes the quantity of the yield and may occasion serious mischief. This is said to be obviated by Castner's process.

ALUMINIUM.

Aluminium, in the form of alumina (aluminium oxide), is one of the most abundant substances on the surface of the earth. It was first isolated by Woehler, by means of the action of potassium upon aluminium chloride

It was for some time obtained only by the decomposition of aluminium-sodium chloride by means of sodium. The double chloride is prepared by treating a mixture of alumina with sodium chloride and tar with chlorine gas, in a retort at a red heat:

$$Al_2O_3 + 3Cl_2 + 3C = Al_2Cl_6 + 3CO.$$

The aluminium chloride is volatilised as the double aluminium-sodium chloride, and is condensed in a walled chamber, lined internally with earthenware. The double chloride is decomposed by bringing it in contact with sodium on the sole of a reverberatory, when there are formed free aluminium and a saline mass, consisting of the double chloride and the excess of sodium chloride, which incloses the metallic aluminium.†

* Weldon calculated the cost of sodium at 7*s*. to 8*s*. per kilo., but the greater portion of this sum is for the destruction of the retorts in which the process was then effected. Castner hopes to be able to produce sodium at 25 cents per lb. He effects the reduction by carbon diffused in alkali, melting at moderate temperatures, or by means of a metallic carbide. Mierzinski and Jablochkoff propose to obtain sodium by the electrolysis of sodium chloride. (See *Aluminium*, by Jos. W. Richards, pp. 130–143.)

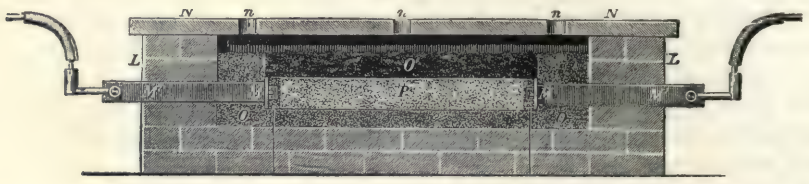
† A modification of this has been worked at Salindres, by A. R. Pechiney & Co., successors to Henri Merle & Co.

The raw material is bauxite. This is first converted into sodium aluminate to get rid of the accompanying iron (ferric oxide). From the solution of the aluminate hydrated alumina is thrown down by a current of carbon dioxide and washed. The precipitate thus obtained is mixed with carbon and sodium chloride, and this mixture is treated with chlorine gas to obtain the double aluminium-sodium chloride which is finally decomposed by treatment with sodium. In this last operation cryolite (the aluminium-sodium fluoride) is added. The production of aluminium at

The process of Cowles Brothers, which calls in the aid of electricity, and which is rather adapted for the production of certain valuable alloys than of pure aluminium, is thus described:—

The inventors use a furnace, *L* (Fig. 220), the iron cover of which, *N*, contains openings, *n*, for the escape of the carbon monoxide evolved. At the bottom is a stratum of powdered coal, saturated with milk of lime, about a hand's-breadth in depth. Over this is spread the mixture to be reduced, *P*, consisting of broken corundum, mixed with fragments of charcoal and the requisite quantity of copper (*i.e.*, for the formation of bronze) in small grains. By means of a rectangular frame of sheet-metal, it is arranged that the coarser materials lie only in the middle. The electrodes, *MM'*, which enter the hearth, serve for the production of a powerful electric arc. They are blocks of carbon, 7·5 centimetres, in square sections of 75 centimetres in length. The furnace itself is 1½ metre long and 0·3 metre broad and deep. After the charge of ore, more charcoal is spread, in the first place, between the wall of the hearth and the sheet-metal frame, and, after its removal as a layer, *O'*, to

Fig. 220.



cover the whole. The furnace is then closed with its cover, and the current is passed through.

According to Mehner, the machine used yields, at 907 rotations, 1575 ampères and 47 volts. To prevent short-circuiting, strong resistances must be inserted at first. In about one hour the reduction is complete. The aluminium bronze at the bottom of the furnace contains 15 to 35 per cent. aluminium. In the layer of carbon above there is said to exist an aluminium carbide. A dynamo of 100 electric horse-power is said to produce in 20 hours 150 kilos. of a 10 per cent. aluminium bronze. A company at Lockport has bought a water-power of 1000 horse-power hours, and expects to produce the aluminium alloys so cheaply that the aluminium contained in them will cost only 3*s.* 6*d.*—a hope which is very sanguine. It is improbable that pure aluminium will be produced in this manner at 4 to 5 shillings per kilo.

According to Maberry, the volatilisation of aluminium in this process may be pre-

Salindres has been from 2000 to 3000 kilos. yearly. The cost per kilo. is estimated at 69¼ francs. For the details of the processes, the reader is referred to Fremy's *Encylopédie Chimique.*

A novelty was the introduction, as a raw material, of cryolite, $Al_2Na_6F_{12}$. Its use is not free from disadvantages, as the yield is relatively small; the crucibles are attacked, and the aluminium obtained is deficient in purity.

Webster's process, used at the Aluminium Crown Metal Works, at Hollywood, turns upon the use of an exceptionally pure alumina. The inventor incorporates three parts pure alum with one part of coal pitch, and heats to 200° or 260°. After treatment, the particulars of which are found in the author's patent, a product is obtained containing 8·41 per cent. of actual Al_2O_3, the cost of which is said to fall below £100 per ton.

From the by-products it was said that a blue dye was obtained which served as a substitute for indigo (!), and was worth 6*s.* per lb. This colouring matter is a Prussian blue, which is of course not without value. Beyond taking this pure alumina as a raw material, Webster's procedures do not seem to involve any novelty. The sodium produced is of excellent quality, but it is too costly for extended uses.

For a number of proposed methods, none of which seem to have achieved any decided success, the reader may consult *Aluminium*, by Jos. W. Richards (pp. 178–189).

vented by the presence of copper, tin, or iron. No electrolytic aluminium has yet appeared in the market.

The process of Prof. Netto is carried out by the Alliance Aluminium Company at Wallsend-on-Tyne.

These works at present comprise four reverberatories, arranged in two blocks, each 23 ft. by 8½ ft. by 9 ft. high. Each furnace is charged from the top with a mixture of cryolite and salt, which when melted is drawn off into a movable iron converter in which the decomposition is effected. Sodium is thrown into the molten mass, which is worked about with an iron dipper, until all action ceases. The slags are then run off into an iron pot, and the aluminium is found in the shape of a "button" at the bottom of the converter. The yield of metal is about 8 per cent. on the weight of cryolite, and three parts of sodium are used to furnish one part of aluminium. The resulting slag, sodium fluoride, on treatment with an oxygen salt of aluminium, forms an artificial cryolite, which serves for the production of aluminium as well as the natural mineral. For producing 1 ton of aluminium there are required 12 tons cryolite, 12 tons common salt, 12 tons coke for heating, and 3 tons sodium. The by-products are 20 tons slag, containing 40 per cent. sodium fluoride, 15 per cent. of undecomposed cryolite, and a trace of clay, the remainder being common salt.

Properties.—Aluminium is greatly modified even by small quantities of other metals. The common commercial metal has a slight bluish-white cast, intermediate between the colours of tin and zinc. But the pure metal is almost absolutely white. It is very malleable and ductile; it can be beaten into leaf as thin as gold-leaf. When cast it is as soft as silver, but by hammering and rolling it is rendered nearly as hard as iron. Its specific gravity at 4° is, when cast, 2·56. According to Deville, it conducts electricity eight times better than iron. The melting-point of the absolutely pure metal is about 650°, but ordinary commercial samples are about 815°. It is probably the most sonorous of all metals.

As regards its chemical properties, it is not oxidised by the action of air or water. Unlike silver, it is not blackened by sulphuretted hydrogen. Nitric and sulphuric acids scarcely affect it, but in hydrochloric acid or in solutions of the caustic alkalies it dissolves readily.

Applications.—From its combined lightness and strength aluminium is admirably adapted for use in watch-making, for the frames of microscopes, spectroscopes, and other delicate optical and physical instruments, and for many surgical appliances. It will probably supersede all other metals for the production of bells, wind instruments, and pianoforte wires. Its high conductive power for electricity, joined to its great lightness, render it preferable to iron and copper for telegraph wires. This is especially the case as regards field telegraphs. An aluminium wire extending three miles will not weigh as much as copper wire of one mile.

Alloys.—The alloys of aluminium are exceedingly important. An alloy of aluminium and iron (Mitis metal) is said to be from 30 to 50 per cent. stronger than the iron from which it is made, and is certainly free from porosity and from enclosed air-bubbles. Even such small proportions of aluminium as 0·2 per cent. greatly improve the quality of iron and steel. "Wasters" are almost unknown to ironfounders who use aluminium, and very thin parts and sharp edges are thus cast with ease.

The aluminium bronzes, containing 2½, 5, 7½, and 10 per cent. aluminium, according to the purpose intended, are both useful and ornamental. For artillery, the 10 per cent. aluminium bronze is the metal *par excellence*, by reason of its hardness and homogeneity, its high breaking-strain, its elasticity, and resistance to corrosion. This 10 per cent. bronze is not changed in its properties how often so ever it is re-cast. It will not only take the place of phosphor-bronze, silicon-bronze, &c., but even of steel for ships' propellers, pistons, cylinders, cogged wheels, engine-fittings of most kinds,

bearings, &c. Mierzinski is of opinion that in any part of a machine which is commonly made of steel, this bronze can be substituted. Its strength when hammered is equal to the best steel. Soldering aluminium and its alloys was for some time a difficulty, but the Alliance Aluminium Co. now supply a solder which works perfectly if the instructions are followed. Aluminium can be welded electrically, and it has the advantage of not clogging files.

MAGNESIUM.

Magnesium, which occurs in exhaustless quantities in sea-water as magnesium chloride and bromide, and in carnallite, as sulphate in kieserite, schœnite, and kainite, and as carbonate in magnesite and the dolomites, has only been included among the technical metals within the last twenty years. It is silvery white; its recent fracture appears either slightly crystalline, finely granular, or even fibrous. It is as hard as calcareous spar, and becomes dull on exposure to the air. Slightly above its melting point it takes fire, and burns to magnesia with a dazzling white light. Its sp. gr. is = 1·743.

It has hitherto been produced exactly like aluminium, magnesium chloride, or carnallite, being decomposed by heating in contact with sodium.

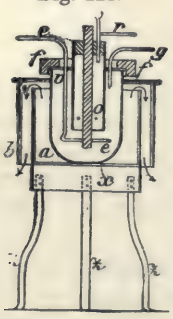
Until recently, it was prepared by the Magnesium Metal Company, at Patricroft, near Manchester (conducted by Mellor); by the American Magnesium Company, at Boston, U.S.A. (producing each 2500 kilos.); and in Paris (about 100 kilos.).

The magnesium of commerce is never pure, as is seen from the following analysis (1872 and 1876). I. is English magnesium, and II. and III. are French samples:—

	(I.)	(II.)	(III.)
Magnesium	96·381 per cent.	92·357 per cent.	93·620 per cent.
Aluminium	0·342 ,,	— ,,	0·216 ,,
Zinc	— ,,	— ,,	3·063 ,,
Iron	0·673 ,,	5·686 ,,	0·101 ,,
Carbon	0·120 ,,	0·091 ,,	0·201 ,,
Silicon	2·309 ,,	1·860 ,,	2·421 ,,

In 1852 Bunsen prepared magnesium electrolytically from magnesium chloride by means of his zinc-carbon elements. As decomposing cell he used a porcelain crucible, 9 centimetres in height and 5 centimetres in width, divided into two halves by a partition reaching down to half-depth. Through the cone were passed the two carbon poles of the battery. The saw-like projections of the negative pole served to hold the separated metal below the melting salt, as it otherwise rises to the surface and ignites. The author was the first to show that fused potassium-magnesium chloride ($KMgCl_3$ carnallite) is very suitable for the electrolytic separation of magnesium, and that its combustion may be prevented by the introduction of reducing-gases.

Fig. 221.



In order to heat the porcelain crucible to a red heat as uniformly as possible, there were used two sheet iron rings, *a* and *b* (Fig. 221) lined with asbestos pasteboard connected below by three strong wires and resting on three feet, *z*. The cover, which is also lined below with asbestos pasteboard, has an opening in which the crucible fits when it rests upon a thick iron wire enclosed in the pipe-clay tube, *x*. If a triple burner is placed below, the hot gases play uniformly round the crucible, as they are compelled by the outer ring, *b*, to re-descend in the direction of the arrows. When the double salt is melted, a round asbestos plate, *v*, is put on and pressed firmly upon the edge of the crucible by the heavy cast iron ring, *b*. The asbestos plate contains an earthen tube, *o*, in which have been bored several lateral

holes. In this earthen tube there is secured, by means of asbestos plates, the carbon which serves as positive electrode, and the tube *r*, with a lateral appendage for carrying off the chlorine. This form of tube was selected to obviate possible obstructions and, after lifting off the plug, to ascertain the development of chlorine by means of a slip of litmus-paper. As negative pole is used an iron wire, *e*, 5 millimetres in thickness, the lower end of which forms a ring round the carbon. Gas is very slowly introduced through the tube *g*; it has been dried over calcium chloride, and escapes with the chlorine through the tube *r*. The magnesium melts in balls of the size of a nut. Graetzel has modified this process by using the iron crucible as a negative electrode, as Davy proposed for potassium.

Considerable quantities of magnesium are now so cheaply prepared by the electrolysis of carnallite that the sodium process can no longer compete.

The technical uses of magnesium are not important. As an illuminating agent it can be thought of only in special cases, for military purposes, &c. A Berlin firm recommends for a white fire, shellac 1 part, 6 parts barium nitrate, and $2\frac{1}{2}$ per cent. magnesium powder. The shellac and the barium salt are melted together and ground. For a red fire the mixture is similar, only for the 6 parts barium nitrate are substituted 5 parts strontium nitrate.

SECTION III.

CHEMICAL MANUFACTURING INDUSTRY.

WATER AND ICE.

WATER occurs as rain-, spring-, river-, and sea-water. When, after sunset, objects upon the earth's surface are cooled down below the dew-point, a part of the water existing in a gaseous state in the air is precipitated upon such objects as dew, in the form of small drops, or as hoar-frost if the temperature be below 0°. If a considerable volume of air is cooled below its dew-point, the corresponding quantity of water is also separated in minute drops, forming mists or clouds. These drops sink down slowly, and if the lower strata of air are warmer and not yet saturated with water, they resume the form of vapour. But they fall down upon the earth as rain—or frozen as snow and hail—if the moisture in the lower strata of the atmosphere approaches the dew-point.

The quantity of the atmospheric waters thus deposited is generally greatest within the tropics and near the sea, and smallest towards the poles. Thus the mean height of the rainfall is at—

Madrid	25 centimetres	London	63 centimetres
Vienna	45 „	Rome	78 „
Petersburg	46 „	Genoa	118 „
Stockholm	51 „	Bombay	198 „
Berlin	57 „	Havanna	231 „
Paris	57 „	St. Domingo	273 „
Hanover	58 „		

The distribution of the rainfall in the seasons is very different. Autumnal rains predominate in Britain, the west of France, the Netherlands, and Norway; summer rains in Germany, Denmark, and Sweden; summer rains are absent in those parts of Europe which lie nearest Africa, *i.e.*, southern France, Italy, Portugal, &c.

The quantity of rain in single years deviates very considerably from the general average. Thus, at Frankfort the mean rainfall for thirty years is 60 centimetres, but in 1864 it was only 36 centimetres, and in 1867, 144 centimetres.

About half this atmospheric water is directly returned to the air by evaporation; the remainder chiefly penetrates into the soil as far as the first impervious stratum along which it flows in accordance with the law of gravitation, and is finally either raised artificially in wells or comes to light in natural springs, and, in conjunction with the surface drainage, is conveyed to the sea in brooks and rivers. Generally a permeable soil and shattered rocks are rich in springs, whilst a compact clay soil and a solid rock formation yield only feeble springs.

Composition.—Rain and snow contain the constituents of atmospheric air, nitrogen, oxygen, carbon dioxide, and also the impurities of the atmosphere in proportion to their respective solubilities. Rain-water collected upon clean surfaces can hence, in many cases, be used in the chemical arts in place of distilled water. Water obtained from roofs is at the commencement of wet weather often contaminated by dust, the

droppings of birds, &c. Water which has been preserved in cisterns, and which in low, swampy, coast districts is used for all domestic purposes, is often very impure.

Among the impurities of the atmosphere sulphurous acid, chlorine, ammonia, and nitric acid are the most important.

Sulphurous acid or sulphuric acid is especially due to coal fires. According to Sendtner freshly fallen snow at Munich contained per kilo. 7 milligrammes total sulphuric acid, the next day, 17·6 milligrammes, in ten days 62·2, and in sixteen days 91·8 milligrammes. Thus snow very quickly absorbs the sulphurous acid existing in the air of towns, which soon passes into sulphuric acid. Such snow or rain is very injurious to statues or monuments of marble placed in the open air. Angus Smith found at Liverpool 35 milligrammes sulphuric acid per litre of rain-water, at Manchester 50 milligrammes, at Newcastle-on-Tyne (among sulphuric acid works) 430 milligrammes, and this chiefly in a free state.

The proportion of chlorine (or of chlorides) is of importance only on coasts.

The ammonia in rain-water is chiefly derived from processes of putrefaction, but also from chimney gases, if the combustion is imperfect. Rain-water generally contains from 0·5 to 5 milligrammes, but sometimes as much as 30 milligrammes per litre. Snow after remaining a long time on the ground contains much ammonia.

Rain-water contains also from 1 to 10, but sometimes even 50 milligrammes nitric acid, due either to the decomposition of organic matter, or formed by electric discharges.

Spring- and Well-Water.—The rain-water charged with these matters penetrates chiefly into the soil when it does not immediately evaporate, and comes up to daylight in springs, or is artificially raised in wells after taking up more or less of the constituents of the strata which it has traversed.

In water it is common to distinguish the carbonic acid into that which forms, with the existing metals, simple carbonates; that which is half-combined, forming, with the carbonates, bicarbonates, and being capable of expulsion by boiling; and that which again is free, and merely dissolved in the water. In some springs, especially in volcanic districts (as the Eifel, the Laach lake, &c.), the water holds in solution carbonic acid, in volumes several times exceeding its own. The ordinary well- and spring-waters owe their carbonic acid in part to the atmosphere, but chiefly to the processes of putrefaction and decay taking place in the soil. Carbonic acid assists in the decomposition of minerals, and forms calcium and magnesium bicarbonates, less frequently similar compounds of iron, sodium, &c., so that ordinary spring-waters contain only a relatively small quantity of carbonic acid in a free state. Well-waters contain, as a rule, no free carbonic acid, but often, in a greatly polluted soil, considerable quantities of calcium and magnesium carbonate, and have, in consequence, a great transitory hardness.

The quantities of lime, magnesia, alkalies, sulphuric acid, &c., vary very greatly according to the nature of the soil. The less variable are the quantities of the products of the decomposition of animal excretions, which in populous places penetrate into the earth to a great depth. Such matters at ordinary temperatures and under the influence of certain microscopic organisms, are quickly resolved into decomposition products as yet but imperfectly known. In presence of atmospheric oxygen they form carbonic acid, ammonia, and then nitrous and nitric acids. The phosphates, the nitrogenous organic matters, and the ammonia are in part retained in the soil, and conveyed to the roots of plants; the chlorides, nitrates, and sulphates are carried away by the water to the wells and springs. These changes take place especially in soils covered with vegetation. Polluted waters after filtering through the soil contain much more nitric nitrogen (nitrogen in the state of nitrous and nitric acid) than they did previously. If nitrogenous organic substances are conveyed into a soil not covered with

plants, then if the access of air is sufficient, the nitrogen of such organic matter and the ammonia which has been formed are quickly converted, firstly into nitrous, and then into nitric acid, which are taken up by the water in the soil, and conveyed into the springs and wells. If sufficient oxidation cannot be effected, from scanty access of air, when the absorptive power of the soil is exhausted, the ammonia and the putrescent organic substances are taken up by the water. Water which springs out of the earth remote from human habitation *may* be perfectly free from decomposing animal products or may contain mere traces.*

The water of wells which reach down into the ground-waters of cities and are partly fed by soakage from the street-sewers, the cess-pits, &c., contains impurities to a serious degree. The proportion of sulphuric acid may reach 1 gramme per litre; that of ammonia 100 milligrammes, organic matter 1 gramme, and chlorine 90 centigrammes. As the latter (except in marine or saliferous districts) is chiefly derived from the sodium chloride of human excretions, its presence gives a valuable indication for determining the character of a well-water.

The composition of river-waters is naturally very different according to the character of the formations which they and their affluents traverse. Sea-water contains especially sodium and magnesium chlorides, calcium and magnesium sulphates; potassium compounds are found only in small quantities. Calcium carbonate is likewise scantily present, often in mere traces; near the coasts it is more abundant. Magnesium carbonate is still more sparingly present.

It is impossible to pronounce a water fit or unfit for domestic uses unless we know its origin and the surroundings of its source. It is by no means indifferent whether the organic matter detected in a sample of water is derived from a peaty soil or from a cess-pit. Here the presence of chlorine, ammonia, and nitrites gives valuable indications. So-called "standards" and limits are only of very local value.

Drinking-water should not be too hard, and its temperature should fluctuate little.

Examination of Waters.—The reader will do well here to consult the following works:—*Water Analysis*, by J. A. Wanklyn and E. Th. Chapman; *Volumetric Analysis*, by F. Sutton (latest edition, the section relating to the examination of water); *Select Methods in Chemical Analysis*, by W. Crookes, F.R.S., p. 657, for estimation of free oxygen in water, and p. 659, for an expeditious method of estimating the temporary hardness.

It is a very prevalent error to say that the colour of water gives little help towards ascertaining its quality. Water free from organic pollution has, if seen in a sufficient volume, a peculiar blue colour. If contaminated with organic matter in solution, it has a brownish or yellowish colour. The process in question, devised by W. Crookes, W. Odling, and C. Meymott Tidy, is, in substance, as follows:—Two hollow glass wedges are filled, the one with a brown and the other with a blue solution. The blue solution is made by dissolving 5 grammes pure crystalline copper sulphate in 1 litre distilled water. For the brown solution dissolve ferric chloride and cobalt chloride in distilled water in such proportions that 1 litre of the solution may contain 0·7 gramme of metallic iron and 0·3 gramme of metallic cobalt. A very slight excess of free hydrochloric acid must also be present. These two wedges are made to slide across each other in front of a circular aperture in a sheet of metal. In this manner any desired combination of brown and blue can be produced. Each prism is graduated along its length from 1 to 40, the figures representing millimetres in thickness of the solution at that particular part of the prism. On a level just below the

* Some savage tribes in Africa and South America have the dreadful custom of burying the bodies of chiefs, &c., underneath a spring, or in the bed of a stream. Water containing no animal pollution may be very dangerous in consequence of decomposing vegetable matter—*e.g.*, the drainage of rice-fields and the waters of mangrove thickets.—EDITOR.

prisms is a 2-foot tube containing the water to be examined, and having in front of it a circular aperture of the same size as the one in front of the prisms. The stand supporting the prisms and tube is placed horizontally in front of a uniformly lighted window. The observer, standing a little distance off, sees two discs, the lower one illuminated by light which has passed through 2 feet of the water, and the upper one illuminated by light which has passed through the respective thicknesses of the brown and blue solutions. By sliding the prisms sideways one way or the other, it is easy to imitate with considerable accuracy the depth and tone of the colour of the lower disc. A metal pointer fixed over the centre of the upper disc shows on the prism scales the number of millimetres in thickness through which the light has passed to produce a colour which corresponds to that of the water, and the results are recorded thus: "February 21st (New River), 20 : 21," meaning that on that date the colour of New River water seen through a 2-foot tube was represented by 20 millimetres of the brown and 21 millimetres of the blue solution.

Purification of Water.—Water requires to be purified in various ways, according to its original condition and the purposes to which it is to be ultimately applied. Sewage and industrial waste waters, which generally occur together, may be treated by irrigation, filtration, or precipitation. For the conditions under which these processes are available, their drawbacks, and the manner of their execution, the reader may consult Slater's *Sewage Treatment and Purification* (Whittaker). The compound processes of precipitation may be considered as "inverse irrigation," as, instead of passing the impure water through the soil, fresh portions of clay, peat, &c., are continually passed through the sewage, and are then caused to subside (carrying with them the impurities they have absorbed) by the addition of a suitable salt of aluminium or iron.

Water for human consumption, for cookery, &c., should be as free as possible from organic matter, and especially from micro-organisms. It is very doubtful in how far this can be effected by any practicable filtration. The celebrated Chamberland filter, used by Pasteur in his researches, effects the end desired, as far as microbia are concerned, but very slowly. Precipitation with lime (see p. 237, Clarke process) removes the germs (pathogenic and other) for a time, but they are apt to reappear if the clear water is allowed to remain standing over the precipitate. From time immemorial the Chinese have been in the habit of adding to the impure water which they use for drinking small quantities of alum, letting the precipitate subside, and drawing off the clear. Since this simple method has been introduced among the French troops in Tonkin, the soldiers have suffered much less from dysentery—a fact proving that alum not merely removes the suspended earthy matters, but is also capable of eliminating dissolved organic matter—as any one practically acquainted with the art of dyeing would expect—and even organisms. Brautlecht (Slater's *Sewage Treatment*, p. 99) even proposes the use of alum for detecting or removing the microbia in water. He adds a few drops of a solution of a salt of aluminium to some of the suspected water, allows the precipitate to settle, decants off the clear, redissolves the sediment in a few drops of acetic acid, and searches for the organisms in the solution thus obtained.

Water for Steam-Boilers.—In deciding on a water for steam purposes it must be considered in how far it may corrode the boiler-plates or form solid deposits (crock). Whilst the destruction of the boiler-plates from without depends on the action of sulphurous acid, and of an excess of oxygen in the flue gases in presence of moisture; injuries to the boiler from within are to be sought for in the composition of the feed-water. Magnesium chloride is especially destructive to the plates, and in sugar-works it is found that treacle has an injurious action on the boilers. Feed-water containing oily and fatty matter is unfit for use.

The chief compounds concerned in the formation of crock are calcium sulphate and calcium and magnesium carbonates.

The calcium sulphate separates according to the temperature and the proportion of saline matter in the water, either as anhydrite or with water of crystallisation; magnesia is deposited as hydrate. Calcium hydrate also forms solid incrustations if, *e.g.*, too much milk of lime has been used in purifying the water. The prevention of crock, which interferes with the heating of the water, is best done in a cistern before it is pumped into the boiler, and may be effected by means of soda. The numerous patented or secret anti-incrustation compositions should be regarded with suspicion, as most of them are of little or no value.

Water for Breweries.—If perhaps too great an influence upon the quality of beer has been ascribed to the character of the water, yet recent experiments have proved that certain constituents of water may act unfavourably upon softening the barley in the mashing and the fermentation.

The use of water containing organic matter in course of decomposition is especially objectionable. The organic matters attach themselves to the malt, carry on their process of decomposition, induce putrefaction and mouldiness, and under certain circumstances may injure the fermentation of the wort obtained from such malt. Tannic, crenic, and apocrenic acids are hurtful. Water from woodlands and from rivers receiving the waste waters of tanneries should be used with caution.* Beer made with water containing animal impurities will not keep. The drainage of the brewery itself exerts an injurious effect upon the process of fermentation.

As regards the first products of decomposition, Lintner points out that as we justly characterise their presence in drinking-water as suspicious, they should be used in brewing and malting only in extreme cases and with caution. A malthouse which, according to Lintner, worked with polluted water, had to contend with the mouldiness of the malt, which disappeared as soon as a different and better supply of water was obtained.

A considerable proportion of magnesia is objectionable. Concerning the presence of lime, opinions are divided, but it has been ascertained that soft water effects the swelling of the barley more quickly than such as is hard. But as soft water dissolves out of the barley on steeping more extractive matter and salts than a calcareous water, greater care is needed with the former. According to Griessmayer, soft water removes from the grain of barley more phosphoric acid and potassium phosphate than does hard water, forming within the grain insoluble phosphoric compounds which are subsequently re-dissolved by the lactic acid of the mash. On the other hand, hard water during steeping causes the formation of insoluble proteine-lime compounds, and thus diminishes the yield of soluble albuminoid matter. A water containing a moderate proportion of lime is decidedly preferable for malting.†

In the subsequent operations, a soft water is preferable, although a gypsiferous water promotes the clearing of the wort.

Water for **distilleries** should be as pure as possible, and should be at a low temperature in summer.

Water for **starch-works** should be especially free from suspended matter, organic excretions, vegetable residues, salts of iron, and algæ.

All these substances may pass through the sieves along with the starch, remaining in it partially in the centrifugal process, and appear in it when dry. The water must be free from ferments and schizomycetes. The former prevent the starch from depositing, and throw it into the so-called flowing state. The others form organic acids, such as the lactic and butyric, which cannot be entirely removed, even by the most prolonged washing, and also give the starch a putrid odour. The warmer the

* Or rather, as far as tan-liquors are concerned, be totally rejected.

† The largest malthouses in England, *e.g.*, those of Hertford and Stowmarket, have sprung up in districts supplied with hard water.

weather the more dangerous is the presence of the organisms of putrefaction. Organic matter and ammonia render the water suspicious, and salts of iron are a total bar to its use.

The water can generally be much improved by the addition of a little milk of lime and warming or filtering.

For **sugar-works,** chlorides are less liable to promote treacle than are the sulphates and alkaline carbonates; especially hurtful are the nitrates, which render six times their own weight of sugar unable to crystallise. The behaviour of the water in steam boilers is also very important at sugar-works, on account of the great demand for steam.

In **paper-mills,** the presence of iron is very injurious, on account of the formation of rust-spots; lime and magnesia weaken the solution of the resin-soap by partial decomposition.

Water for **tanneries** should contain no putrescent organic matter, as this causes the leather to decay. Eitner's experiments prove that free carbonic acid and water containing bicarbonates swell the hides; chlorides do not unite with the hides, and even counteract the swelling effect of acids. Hence sea-water is unfit for tanning. Calcium and magnesium sulphates are especially good for swelling the hides. This explains the advantageous action of a careful addition of sulphuric acid to a water containing an abundance of bicarbonates.

The finished leathers resulting from these experiments were quite in accordance with their appearance after swelling. The specimen which had been treated with magnesium sulphate had the finest cut, and next came that with sulphuric acid. Samples with distilled water, or with bicarbonates, differed respectively little, that with calcium carbonate being the worst. All these leathers were very firm, full, with a compact grain, and the cut surface was smooth and shining. Samples from salt and magnesium chloride were thinner than the above, and comparatively soft; the fibrous texture was finer.

In the manufacture of **glue,** it is found that the extraction of the raw materials (parings of hides, &c.) is far more complete with soft than with hard water. A glue boiled with hard water does not re-dissolve clear after being once dried up.

For **bleach- and dye-works,** water should be perfectly clear and colourless, containing especially no iron.

If a water contains so much organic matter as to be distinctly coloured, if used for bleaching wool it occasions stains in the goods. If iron is present, then on treating the wool with soda, ammonia, or lant, the iron is fixed on the fibre in the state of oxide, or if soap is used as an iron-soap. Iron-water in the flot has a very injurious effect upon the tones of the colours, so that it cannot be advantageously used even for dark shades. Iron-waters are not less injurious in other dyeing and printing operations and in bleaching.

Hard waters do not bleed the dye-wares freely, and often modify the tone of the colours produced. For all bright and light shades they are injurious, though in sad shades or in blacks they economise the dye-ware. But it is easier to render a soft water hard for any particular purpose than to soften a hard water. Hard waters, as a matter of course, decompose soap.*

Madder and its preparations form an exception to most colouring matters in their behaviour with hard waters. As far back as 1791 J. M. Haussmann observed that in turkey-red dyeing fiery tones can be produced only with calcareous water. According to Kielmeyer, grain-reds and mock-crimsons (peach wood, &c.), whether in cotton or wool, take a bluish tone in hard water, which greatly interferes with their brightness.

* Compare Slater, *Manual of Colours and Dye Wares*, p. 221. Crosby Lockwood & Co.

The genuine old madder red and rose as well as the modern alizarine red and rose do not escape the action of calcareous water (?). On the contrary, coralline red, generally so fugitive upon wool or cotton, is not affected by calcareous water, just as coralline reds upon wool resist a frequent soaping much better than do grain (cochineal) reds. The influence of calcium and magnesium carbonate in the water is especially shown when the wet goods are dried in the stove or on the hot-flue. The carbonates remaining along with the water in the wet tissue act upon the red like a feeble alkali, giving it a bluish cast and thereby darkening it. Hence it is prudent to dry such ware spread out as much as possible in a cold room. But the carbonates remain in the air-dried goods and have still the opportunity to act upon the colours on hot pressing or calandering or passage over the drum. If the dyed woollen goods after washing but before drying are taken a few turns through a water slightly soured with acetic acid, or if (in case of cotton goods) a small quantity of acetic acid or of alum water is added to the dressing, the action of the alkaline earths upon reds will be counteracted. According to the investigations of Rosenstiehl a certain proportion of lime is absolutely necessary for madder, garancine, and alizarine dyeing. The alizarine and the purpurine must encounter in the water of the dye-beck so much neutral calcium carbonate or acetate that there may be formed under all circumstances monocalcium alizarate or the corresponding purpurine-lime lake; the latter is not absolutely necessary, but it contributes to the fastness and brightness of the colour produced. In order to render the excess of calcium carbonate in a spring-water harmless in dyeing oxalic acid seems to be the most serviceable agent; it is used in some works for correcting the water, whilst in others acetic or sulphuric acid is employed, though, according to Kielmeyer's observations, with very unsatisfactory results. The oxalic acid added to the flot, even though accurately calculated, strips a part of the mordant from the cotton prior to the formation of the calcium oxalate, thus producing uneven colours and soiled whites. For soap-baths oxalic acid is the best corrective. Here it can be added along with potash to the hot water; the insoluble calcium oxalate is formed at once before the soap is added, and the latter finds no more lime in the water which could permit of the formation of a lime-soap. If a soap-bath has to be often renewed and used only for a short time, this method of purifying the water is the most suitable. The purifying of soap-becks with potash alone without the additional oxalic acid cannot be recommended, as it is dangerous for the colours. For large soap-becks, for raising-pans which have to be set afresh only once or twice daily, the water is boiled up first with a small portion of the soap; the lime-soap first formed is carefully skimmed off, and the soap is then added to the water thus purified.

In cleansing wool and woollen goods lime and magnesia are injurious, not merely by rendering a part of the soap ineffective, but because the lime-soap formed cannot be easily removed from the fibre, and on subsequent treatment with the mordant and the colouring matter it occasions a number of irregularities. In washing wool with soda, ammonia, or lant, lime and magnesia are less injurious, as any carbonates deposited upon the fibre are more easily removed than lime and magnesia soaps.

The constituents of water have a remarkable influence in the treatment of raw silk. It is universally recognised that the silk thread, as spun by the caterpillar, is coated with a varnish or "gum," which dissolves in boiling soap-lye. During this treatment, according to L. Gabba and O. Textor, the colouring matters of the silk are extracted also. Cocoon silk, on repeated boiling with soap, loses 22·26 per cent. and raw silk 20·14 per cent., so that on unwinding the cocoon threads in hot water 2·12 per cent. of organic matter is lost. But these portions give the raw silk its appearance, its colour, and its strength, and hence they should be retained in the raw silk. In order to render the reeling of the cocoons possible, the natural gum should be softened, though not dissolved, as it must cement the single cocoon threads together so as to give

strength to the raw silk after hardening. The strength of the silk decreases exactly in proportion to the loss of soluble matter, whilst the elasticity is affected only in a secondary degree. As the cocoons are softened in hot water to facilitate reeling, and are kept floating during this operation for convenience, it appears likely that the composition of the water must not be without influence upon the character of the silk obtained.

In fact, comprehensive experiments have shown that silks spun in soft waters were less fine in colour or less strong than those which had been obtained in hard waters. The reason is that the soluble matters which ought to be retained are more readily dissolved by soft than by hard waters, and are thus removed from the silk.

Investigation has further decided that silks spun out of waters rich in lime and alkali give the best-looking products; therefore the producer of raw silk gives a preference to the use of hard water. But for the silk-manufacturer, and especially for the silk-dyer, the silks spun out of hard water are not the most advantageous, as they always contain lime mechanically enclosed. The lime can be shown by an analysis of the ash—the harder the water in which the silk was spun the greater are the quantities of lime found. This inclosed lime cannot be removed on boiling the raw silk preparatory to dyeing. Wherever particles of lime adhere to the fibre the colouring matter of the flot will be taken up less perfectly, and the silks will appear stripy—a very important defect in unloaded, *i.e.*, honest, silks. For bright shades the dyer will therefore give the preference to silks spun in soft waters.

Water for Municipal and Domestic Supplies.—In the use of soap, whether in the household or in manufactures, the proportion of lime and magnesia in the water is of capital importance.

It is well known that soap does not give a clear solution in cold water, but is separated into a soluble, more basic portion and a more acid part insoluble even in alcohol. According to Fricke, these parts had the following respective composition in an experiment made with a good curd soap :—

	Soap.		Insoluble.		Soluble.
Fatty acids . . .	89·55	...	91·36	...	86·51
Soda	10·45	...	8·64	...	13·49
	100·00	...	100·00	...	100·00

The insoluble part contained chiefly palmitic acid, and the soluble part oleic acid. The insoluble part seems to be perfectly inert, at least in cold water; the soluble part on agitation in pure water forms a foam whose numberless vesicles during washing take up the dirt and remove it from the articles to be cleansed. This result can occur only when the soap-lye froths, and is possible only when the existing lime and magnesia salts have been eliminated as insoluble, smeary compounds of fatty acids. In the decomposition 31 parts of soda and 47 parts of potassa are replaced by 28 parts of lime or 20 parts of magnesia, so that 1° of hardness destroys about 120 milligrammes of good curd soap, or 1 litre of a water at 25° hardness 3 grammes of soap; 1 cubic metre of the same water consequently destroys 3 kilos. of soap.

But it is not merely the direct waste of soap which here comes into play; the lime and magnesia soaps formed obstruct the pores of the skin in washing, and deposit themselves in the fibres of washed goods, especially woollens, which consequently lose their softness and acquire an offensive smell. A calcareous or magnesian water, therefore, before being used for fulling cloths, wool-scouring, &c., as well as in the laundry, should be heated with the proportionate quantity of soda to 80° or 100° and should then be decanted away from the sediment. The same treatment removes the compounds of iron and manganese, which not merely destroy soaps, but occasion most unpleasant stains.

That vegetables cannot be boiled tender in water containing much lime or magnesia, but remain hard, is a fact which has been known for above a century and which first gave such waters the name of "hard." According to the experiments of Ritthausen, there is formed in peas boiled in hard water a compound of legumin with lime or magnesia which hardens, on boiling, to a horny consistence. Similar unpleasant effects are noticed on boiling other vegetables and meat in hard waters. It is also well known that much better tea and coffee can be prepared with soft than with hard water.*

Water used for *baking* should contain no putrescent matters which interfere with the fermentation. The water of a brook near Hanover which had been used for many years in baking yielded a perfectly useless paste as soon as it was polluted by the waste waters of a sugar-works.

Pettenkofer and Harz suggest the possible contamination of our dwellings by the use of *bad water in washing the floors*, &c. The same caution must be kept in mind when the streets are sprinkled with polluted waters.

In the construction of houses the quality of the water used for slacking lime, mixing mortar, and steeping bricks is important. Bricks often display whitish, yellow, green, and even black eruptions. The white efflorescences consist of calcium, magnesium, or sodium sulphates, sodium chloride or bicarbonate, which have been originally present in the clay and have been introduced by the water used in building. The green eruptions on light-coloured stones are mostly algæ; black spots such as may be observed on the Berlin Synagogue are fungi which attach themselves only where efflorescences of calcium carbonate and sulphate appear on the stones. In rainy weather such of the above salts as are soluble deliquesce, rendering the walls damp and spotty; in dry weather they effloresce, loosen the plaster by expansion and crystallisation and cause it to peel off. Still more objectionable are calcium and magnesium chlorides, which if once introduced can scarcely ever be removed. The ceilings sooner become grey, as the dust clings more readily, and the wall-papers become spotty.

The custom of filtering impure turbid water, in the erroneous opinion that clear water is always pure, was known to Pliny. The media used for filtering are wool, sponge, cellulose (Piefke), spongy iron (Bischof), unglazed porcelain (Chamberland), asbestos, plastic carbon, silicated carbon, and innumerable others.

As a specimen of a small domestic instrument of this kind the high-pressure filter recently introduced by Glover may be mentioned. The water enters by the cocks *A* and *C* (Fig. 222), passes into the ring-shaped space, *G*, through the filtering material, *F*, and flows out at *D*. In order to remove the deposit of mud the water may be caused to flow for a short time in the opposite direction by closing the cocks *A* and *C* and opening *B*, so that the dirt is carried off by lateral openings. In judging filters it must be considered that the organic impurities contained in the water filtered can be diminished only by absorption and oxidation. The absorptive power of filtering materials, with the exception of animal charcoal, is inconsiderable.

Even this last material does not retain its absorbent powers for ever, and a time comes when it may pollute instead of purifying water passed through it. Oxidation, as it takes place naturally in the earth, is possible only with an abundant access of atmospheric oxygen. But if the filter-bed is constantly covered with water, or if it is closed up, only the oxygen dissolved in the water itself can be transferred to the organic matter—of course a limited quantity.

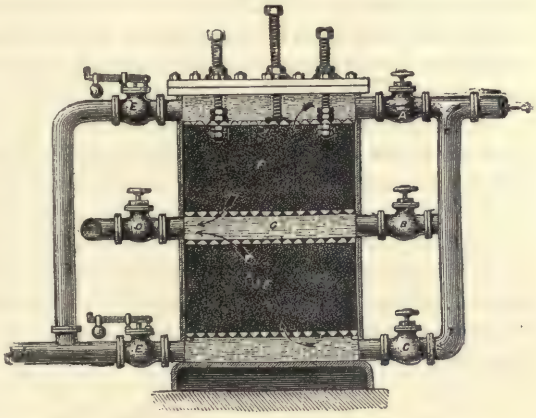
Hence follows a necessity for the frequent airing and purification of all household filters. If this is neglected the water is not improved by filtration, but deteriorated. Filters containing organic matter, cotton, felt, wool, sponge, &c., cannot be recom-

* As regards tea, this dictum may be questioned; soft water extracts more readily and abundantly the tannin of the tea, thus rendering the infusion less pleasant and less wholesome.—EDITOR.

mended, as they promote putrefaction. The recent demand that organic germs should be removed from the water is fulfilled by some; but their performance is very slight.

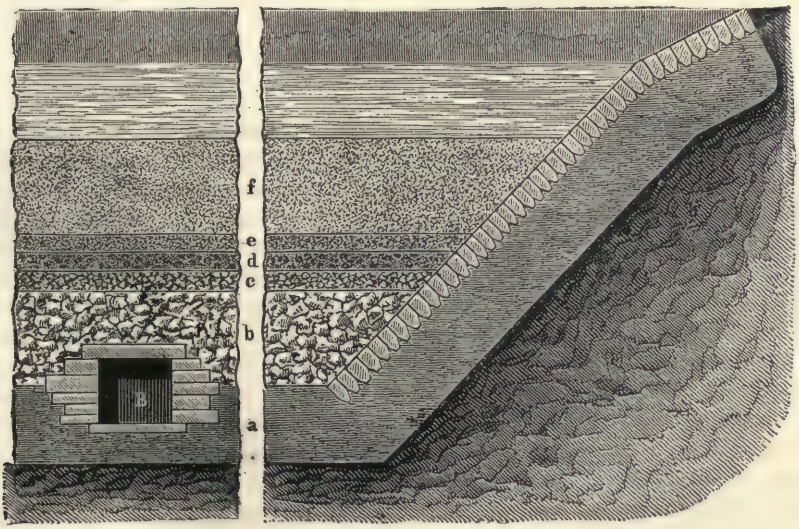
For filtering the water-supply of entire cities large sand-filters are used. Fig. 223 shows the section of the filters erected in Dublin in 1869. The bottom of the filters consists of a bed of puddled clay $\frac{3}{5}$ metre in thickness, a, built in with stones $\frac{1}{5}$ metre in thickness. The filter-materials laid directly upon the clay-bed consist of $\frac{3}{4}$ metre of coarse, angular stones, b, 15 centimetres of smaller stones, c, the same depth of coarse gravel, d, the same depth of fine sand, e, and $\frac{3}{4}$ metre (75 centimetres) of sand, f. To collect the water there are two channels, B, situate half in the bed of clay and half in the stratum of large stones. Each channel is 75 centimetres in width and 60 centimetres in depth. The surface of sand in each metre is 61 by 31 metres; the depth of the water is 60 centimetres.

Fig. 222.



The speed of filtration varies in the existing sand-filters from 1·4 to 15 metres per twenty-four hours. Each water requires, if it is to be well filtered by a given kind of sand, a determined speed of filtration. Thus, under otherwise similar conditions, 3·5 cubic metres of Thames water may be filtered in twenty-four hours per square metre of filtering surface, but only 1·7 cubic metre of Elbe water, as the latter contains much more finely divided dirt. In

Fig. 223.



a well-managed filtration the turbid water passes so slowly through the sand that each of the fine particles of dirt, though far smaller than the intervals between the grains of sand, has opportunity to attach itself to one of the grains. Therefore, the finer and more numerous the particles of dirt are, the finer must be the sand and the slower must be the rate of filtration. If this rate is too great, the sus-

pended particles flow simply through between the grains of sand. But if the sand is too fine, the filter-bed may easily become water-tight, whilst if the sand is too coarse slower filtration is to some extent a remedy. The best size of the sand grains is from $\frac{1}{2}$ to 1 millimetre, and the sand is the better the more uniform the grains are. A sand containing much finer grains cannot be used, as it is easily rendered too compact by the pressure of the water.

For the better preservation of the filter it is requisite that the suspended dirt should remain in the upper stratum and not penetrate into the lower layers. This easily happens at first after cleaning, as the surface of the sand is then very loose. In a newly cleaned filter the head of water should therefore be very small. When once a film has been formed over the surface the pressure may be raised to 1 metre; higher pressures easily break up the bed.

If its performance has become too slow, the filter is allowed to dry, and the upper layer, of about 1 centimetre in thickness, is taken off and washed. There is often, especially in summer, formed upon the filter a layer scarcely 1 millimetre in thickness, consisting almost entirely of Diatomaceæ (Pleurosigma, Synedra, &c.), and rendering the cleansing of the filter necessary on account of their impermeability.

The effects of this sand filtration are confined to a partial oxidation of the dissolved organic matter, and the separation of the suspended matter. The organic germs are especially said to be kept back. According to Koch, filtered water should not contain more than 300 germs per c.c.:—

Day of Examination.	Stralau Works. Spree Water.		Tegel Works. Lake Water.	
	Unfiltered.	Filtered.	Unfiltered.	Filtered.
1885 June 2	5,475	42	118	16
„ 9	7,980	22	117	39
„ 16	6,100	33	115	76
„ 23	6,100	41	1,325	194
„ 30	4,400	53	880	44
July 7	3,500	28	sample lost	42
„ 14	7,200	200	1,896	120
„ 21	110,740	1,656	13,320	49
„ 28	2,640	54	1,500	48

In filtration through perfectly clean sand the swarms of bacteria are only at first a little checked in their forward movement, but they afterwards become more numerous, so that the filtered water sometimes contains more germs than the unfiltered. The imperfection of the action slowly disappears. Sands not sterilised act better at the very outset, and among such those are preferable which have for some time taken part in the filtration in a large tank. Externally such sand was perceived to be no longer sharp, but smeary to the touch. If examined under the microscope, it was found that the single grains were more or less completely coated with a dirty layer which was readily destroyed by heat, and contained a little ferric oxide along with organic matter. That this coating consisted chiefly of bacteria and their germs was plainly shown on bacteriological examination. If a sample of sand was taken from any of the filters, well rinsed with sterilised water, and the rinsings subsequently examined, bacteria were found in enormous numbers. The entire stratum of sand was infected with them, though their distribution was very unequal, decreasing from the surface rapidly at first, and afterwards more and more slowly. As an example, we may refer to a large sand filter, which had been in use for a year and a half. The thickness of the residual bed of sand was 30 centimetres. On cleansing the filter, there were found, per kilo. of sand:—

1. From a dirt heap	5028	million germs
2. From surface of clean filter	734	„
3. From 10 centimetres depth below surface	190	„
4. From 20 centimetres depth below surface	150	„
5. From 30 centimetres depth below surface	92	„
6. From fine gravel below sand	68	„

The residue left on the surface of the sand after the filtration of Spree water is, by reason of its peculiar composition, almost exclusively of organic matter, to be regarded as a culture medium in which the introduction of germs keeps up a process of putrefaction, regulated according to the temperature. The first result is a great increase in the micro-organisms. Many of them are endowed with the power of motion; others with the property of liquefying any gelatinous nutrient matter. They are, therefore, able to break off their connection with their covering of dirt, and to leave it in great numbers. Nothing further stands in the way of their forward movement. The sterilised sand cannot arrest them; nothing clings to its smooth grains, and thus we understand the phenomenon, at first so puzzling, that in filtering Spree water for a long time through sterilised sand, we do not find a decrease of micro-organisms. Upon a filter perfectly sterilised by strong heat, and filled up with sterile water, Spree water was poured, and its filtration was commenced after standing for one day. There were found germs capable of development:—

	Before Filtration.	After Filtration.		Before Filtration.	After Filtration.
2nd day	13,500	97,900	12th day	1,320	29,900
6th „	13,860	205,000	16th „	1,803	4,928
10th „	3,120	17,825	22nd „	1,120	2,356

Results of this kind cannot happen after the sand has become slimy. For as soon as the micro-organisms have left their focus, the covering of dirt, they enter regions which are for them almost impassable, since they present everywhere points of attachment. With few exceptions, they cannot penetrate deeply into the sand, and collect in the upper layers in vast multitudes. Hence the question as regards the admissible speed of filtration acquires a new significance; we must not let the stream become strong enough to wash away any great number of germs from the layers of sand. The question now is, how far we are to take the demands of public health into consideration. If we insist upon the greatest possible freedom from germs the rate of filtration must not exceed 30 millimetres hourly. If we are content with results like those effected at Stralau works, we may admit 60 to 80 millimetres. But to go beyond 100 millimetres would be admissible only under conditions which would be presented by new works constructed with great care.

However important is the elimination of germs, it must not be forgotten that we are unfortunately not always in a position to distinguish the germs of specific diseases from others which are harmless. When, therefore, no water from unimpeachable springs or deep wells is at hand, it is advisable always to boil water before use, even if it has been filtered.

Softening Water.—The Clarke Process.—For softening waters intended for technical purposes the following methods may be adopted.

On heating water, the calcium and magnesium bicarbonates are decomposed, the so-called half-combined carbonic acid escapes, whilst calcium and magnesium carbonates are precipitated, only about 35 milligrammes calcium and 100 milligrammes magnesium carbonate remaining in solution. The so-called temporary hardness of the water is thus much reduced. Movement promotes the separation. If the water contains iron as ferrous bicarbonate, it is separated out as ferric hydroxide.

If steam is available, as is generally the case in manufactories, it may be advan-

tageously brought into direct contact with the water as in Fig. 224. The steam enters through the pipe e, and the part not condensed escapes by the pipe f. The water entering at the pipe c flows if the cock, b, is properly turned over the plates, d, and escapes, when purified, at g.

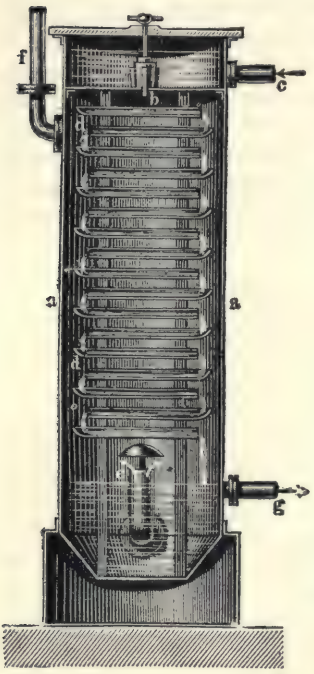
The same result is obtained by the addition of milk of lime:

$$H_2Ca(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

At the same time the magnesium bicarbonate is decomposed with the separation of magnesium hydroxide.

A well-water, which had to be used for feeding a steam-boiler, and for brewing, was heated to 40° to 50° by the waste steam of a steam-engine. It was then mixed in an open cistern, holding 6 cubic metres, with a quantity of slacked lime (ascertained by previous experiments), made up to a stiff paste, the whole thoroughly stirred up and used after the precipitate had settled. The analysis of this water before (I.) and after (II.) the treatment with lime, showed the following composition per litre:—

Fig. 224.



	I.		II.	
Chlorine . . .	152	...	153	milligrammes
Sulphuric acid . .	216	...	208	,,
Nitric acid . .	71	...	70	,,
Nitrous acid . .	trace	...	trace	,,
Ammonia .	slight trace	...	0	,,
Organic matter .	51	...	28	,,
Lime . . .	322	...	172	,,
Magnesia . . .	45	...	7	,,
Precipitable on boiling—				
Lime . . .	176	...	trace	,,

Care must be taken that an excess of lime is not introduced, as water so treated forms a bad crock.

The method of purifying waters with magnesia, as proposed by Bohlig, is expensive, questionable for steam boilers, and for other purposes worthless.

The action of caustic soda is similar, but the sodium carbonate formed decomposes simultaneously a corresponding quantity of the other calcium salts. In most cases the use of sodium carbonate is the more advantageous. Calcium sulphate is decomposed with sodium carbonate as follows:—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

The reaction with the other calcium and magnesium compounds is similar; these metals are precipitated as carbonates with the simultaneous formation of easily soluble sodium salts. If the water contains a large quantity of bicarbonates and of magnesium compounds, the cistern, A (Fig. 225), made of boiler plate, and holding from 2 to 8 cubic centimetres, is run half full of water, which, if practicable, is previously heated from thirty to forty minutes by the waste steam of the engine. The quantity of slacked lime necessary for the entire precipitation is then added (preferably in the form of a stiff paste), and the weighed quantity of sodium carbonate; the valve, b, of the Körting blast, B, is then opened, so that the air drawn in at a, and escaping from the perforated tube, i, may mix the liquid thoroughly. The rest of the water is run in, and after about five minutes the blast is cut off. In from ten to twenty minutes the water becomes perfectly clear. The clearing is expedited if a portion of the precipitate from former operations is left in the cistern.

The softened water should turn good red litmus-paper blue in about twenty seconds,

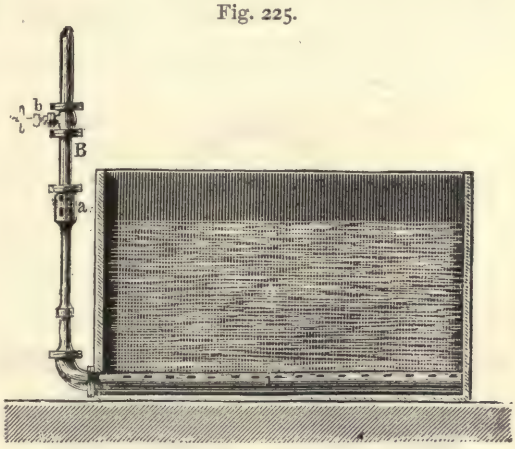
and should give only a very slight turbidity with oxalic acid. It is then not merely fit for steam purposes, but for washing, cooking, brewing, and other technical uses—an advantage not shared by other methods.

According to the process of E. de Häen, water is mixed with the proportions of barium chloride needed for precipitating the sulphuric acid:

$$CaSO_4 + BaCl_2 = CaCl_2 + BaSO_4.$$

Milk of lime is then added to dispose of the bicarbonates. The proposal has given satisfaction for the feed-water of steam-boilers, as the formation of crock is thus prevented; for other purposes it is not applicable.

Fig. 225.



In comparing the cost of these precipitants it must be remembered that 80 parts sulphuric acid (SO_3), or 136 parts calcium sulphate require 208 parts barium chloride or 106 sodium carbonate for decomposition. At equal market prices for both precipitants, barium chloride is therefore twice as expensive as soda.

Distillation. — The removal of the mineral and other non-volatile impurities of water by distillation is especially important for chemical processes and for the water-supply of ships. On the small scale, this is generally effected by means of a copper still, the vapours, as they ascend, being condensed in a worm kept cool by means of water. A violent ebullition of the water is to be avoided, lest particles of water are carried over mechanically and find their way into the receiver. Further, the water which passes over first contains any ammonia which may be present. The distillation must also not be carried to the end, as otherwise the organic matter present and certain salts will be decomposed. In order to obtain water as near as possible of an absolute purity, it is first mixed in a still with potassium permanganate and a little caustic potassa and heated to boiling in a still. As soon as the water boils the fire is reduced, to prevent the liquid—which froths much at first—from boiling over, and the boiling is then continued in the ordinary manner. After about $\frac{1}{20}$ of the water has been evaporated, the condensed water obtained is free from all foreign matter, organic or inorganic, if the worm is fitted with an arrangement to keep back water from being carried over mechanically.

To purify sea-water by distillation, it must be remembered that very little fuel should be used, that the apparatus must take up only a small space, and that the water obtained must be rendered in some measure palatable by the removal of the so-called "still-taste." The ships of the German Navy are provided with stills which can furnish daily from 1·25 to 5 cubic metres of distilled water. As shown in the two sections (Figs. 226 and 227), supposed to be at right angles to each other, the apparatus consists of two cylinders, A and B, 0·4 metre in width. The steam for heating, which is produced in a special boiler, passes through the pipe d, into the net of tubes of the cylinder A, surrounded by the water which is to be distilled. The condensed water collects in the recipient, e, and flows from here, the steam being kept back, into g, from which it is let off by a cock, if it is to be used hot, whilst the rest flows through the tube v, to the refrigerator, o.

The level of the water to be distilled is observed by a gauge. It is previously heated in the cooling vessel, B, and flows through the tube l, in such a manner that

the steam formed must first pass over the copper sieve-plate, a, and then impinge on the plate, c, in order to get rid of any sea-water which might be carried over, before it arrives, through the tube m, at the tube-refrigerator, n. The water may be either let off directly, or may pass through a filter filled with animal charcoal.

The requisite condensing water enters by the tube i, and flows off through k, after the portion required for distillation has been conveyed away. The air which escapes on heating from the condensation water is conveyed, through the pipe t, into the steam-chamber of the distilling apparatus, so that it may dissolve in the water condensed here from the steam, and render it palatable. Through g the steam of the steam-pump is caused to enter.

Fig. 226.

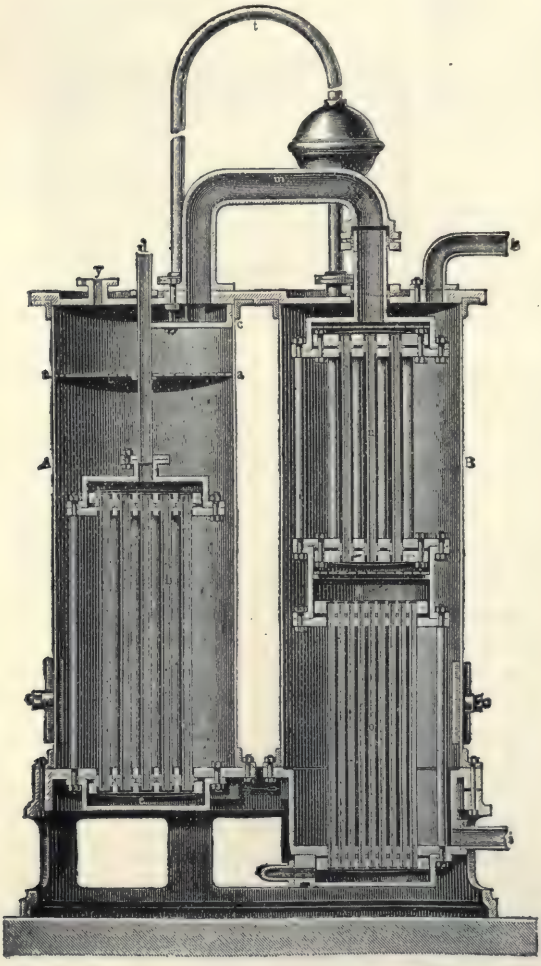
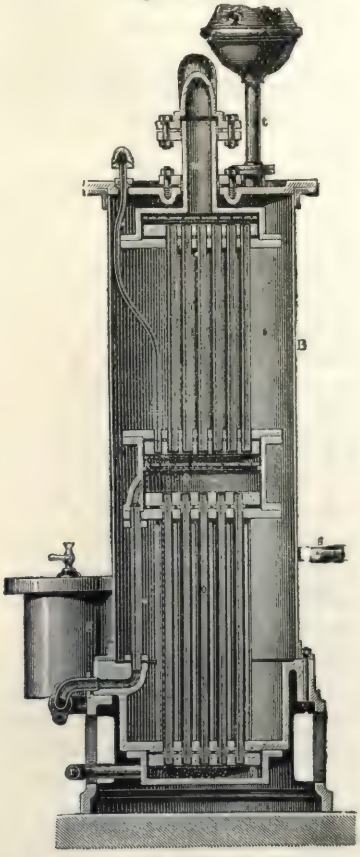


Fig. 227.



Water Mains.—Good water mains must be chemically and physically as inactive as possible. They must not impart to the water on its transit any hurtful (poisonous) metals or unpleasant properties (decayed wood), and they should not be attacked and destroyed either by the water, by the moisture of the soil, or by any other external agencies. A low power of conducting heat is also desirable, so that they may resist both the heat in summer and the cold in winter. Water pipes must be perfectly tight, and must be able to withstand both internal and external pressure.

Wooden pipes are apt to give the water an unpleasant taste, and they are not durable.

Mains of paper, saturated with coal-tar or asphalt, are said to be durable, but they have not come into extensive use.

Earthenware pipes may be recommended where there is no danger of shocks or of excessive pressure.*

Cast-iron mains must be tarred whilst hot, as they may be otherwise much obstructed by rust, or may be corroded. Iron pipes coated with zinc answer well with some waters, but in presence of chlorides they are corroded. Iron mains have also been lined with certain enamels.

For conveying the water into and within houses tin pipes are very good, but too costly.

Lead piping is more generally used in houses. It was employed by the ancient Romans, who, however, observed that lead is sometimes attacked by water.

Lead pipes should be protected from contact with lime and cement, by which they are rapidly destroyed. Water dissolves lead if it contains free carbonic acid or ammonia; chlorides, nitrates, and organic acids promote the corrosion of lead, but calcium carbonate or dissolved silica prevents the attack. Lead pipes are sometimes attacked by water when first laid down, but there is soon formed an insoluble inner layer which protects the metal from further attack. As a rule the use of lead piping seems free from objections; the decision when and where they may be used with safety must depend on an analysis of the water.†

ARTIFICIAL MINERAL WATERS.

Among the substances used in the production of such liquids, the water itself is of the greatest importance. Those intended for medical use should be prepared from distilled water only. Those which serve merely as beverages may be made from an irreproachable drinking water.‡ Certain ignorant or reckless manufacturers use impure well- or river-waters if near at hand. It has been proved that the schizomycetes of Selters waters (commonly called Seltzer) remain capable of development even after the lapse of seven months.§ The carbonic acid must be pure. According to the equation: $MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2$, 84 grammes magnesite and 98 grammes sulphuric acid yield 120 grammes magnesium sulphate, or 246 grammes Epsom salts, and 44 grammes or 22·3 litres carbonic acid. The same quantity of carbonic acid is obtained from 100 grammes pure marble or pure chalk, whilst of dolomite there are needed 90 to 95 grammes. In the choice of carbonates it must be considered that magnesite yields far the best carbonic acid; marble sometimes, dolomite often, and chalk always contain organic matter which gives the carbonic acid an unpleasant smell, and which can only with difficulty, if at all, be removed by the use of potassium permanganate and carbon. The development of carbonic acid from magnesite and sulphuric acid is the most regular. Chalk and marble must be finely pulverised and well stirred up if the decomposition by sulphuric acid is to be at all complete. Magnesite only requires a free room of 50 per cent. of the entire capacity of the generator to prevent overflowing, whilst chalk needs fully 75 per cent.

The sulphuric acid used must be free from arsenic, and must contain neither sulphurous acid nor the nitrogen oxides.

The manufacture is generally effected by saturating water (mixed with the

* Glass mains have been tried experimentally, and may possibly prove successful.

† Gutta-percha pipes are free from objection from a sanitary point of view, and are less likely to freeze in winter than those of lead or tin. But when alternately wet and dry they gradually lose their cohesion, and, like those of lead, they are sometimes attacked by rats.

‡ Such, *e.g.*, as that of Loch Katrine, or the Clarkised Chiltern Hill water.

§ Very bad mineral waters have been exported to India.

necessary ingredients) with carbonic acid. This is done under pressure in appropriate apparatus, and the mineral water, when ready, is at once filled into bottles which are closed air-tight. The carbonic acid gas is either forced into the water by pumps, or it is generated in closed apparatus and driven in by its own pressure. Latterly liquefied carbonic acid has been used with advantage.

It must be remembered that all the beverages containing carbonic acid should be kept from contact with lead or copper vessels, unless well tinned, as they will otherwise dissolve considerable quantities of the poisonous metals.

Ice.—Ice, or some form of artificial cold, is indispensable for breweries, paraffine works, for the production of Glauber salts from the mother liquors of littoral salines and Stassfurt salts, and for many other installations. Natural ice is often plentifully stored with bacteria, and artificial ice should therefore be substituted if possible.

There are two processes—change of the condition of aggregation, and expansion of volume—by which heat is taken up. Hence we may produce cold in the three following manners:—

1. By liquefaction of a solid by means of a liquid (solution of salts) or of another solid (salt and snow)—that is, by means of so-called freezing mixtures.
2. By converting a liquid body (ether or ammonia) into a gaseous condition.
3. By the expansion of compressed air.

The two latter procedures only can come into question on a large scale, though mixtures of snow with dilute acids may be made to produce intense cold on a small scale. In this manner Faudel obtained a temperature of $-60°$ with sulphuric acid of 65 per cent. which he had caused to ascend through a cooling-tube within a column of snow and to flow out at the top.

Evaporation Ice Machines.—The-boiling point of liquids depends on the pressure of the atmosphere or gas which rests upon them. If this is reduced the temperature at which the liquid evaporates is reduced also. If no heat is conveyed from without, that needed for gasification must be taken from the liquid itself, and its temperature must fall the lower the less the pressure and the lower its boiling-point. The following table shows the relations of the bodies which here come into question.

Pressure in Atmospheres.

Temperature.	Carbonic Acid.	Sulphurous Acid.	Ammonia.	Methyl-chloride.	Methyl-ether.	Ethyl-ether.
$-80°$	1·0	—	—	—	—	—
-20	19·9	0·6	1·8	1·2	1·2	0·09
-10	26·8	1·0	2·8	1·7	1·7	0·15
0	35·4	1·5	4·2	2·5	2·5	0·24
$+10$	46·1	2·3	6·0	3·5	3·4	0·38
$+20$	58·8	3·2	8·4	4·8	4·7	0·57
$+30$	73·8	4·5	11·5	6·5	6·3	0·80

Hence, the greatest cold is to be produced with liquid carbonic acid; then follow ammonia, methyl-chloride, and methyl-ether; next sulphurous acid, whilst ethyl-ether produces cold only under a reduced pressure.

Still less favourable is water, which at $0°$ has a tension corresponding to 4·6 millimetres of mercury, and can consequently be cooled down to $0°$ only in an almost complete vacuum. Still, of late, large ice machines have been constructed in which water is frozen by rapid evaporation. To effect this the air is drawn off as far as possible from the containing vessels, and the watery vapours formed are absorbed by concentrated sulphuric acid.

The machines with liquid ammonia, sulphurous acid, and carbonic acid are the most important. They consist, as it is diagrammatically shown in Fig. 228, mainly of the evaporator, A, in which the liquid concerned vaporises and withdraws the

requisite heat from the solution of magnesium chloride circulating in the pipes. The pump, B, draws the gas, forces it into the cooler, C, in which it is again liquefied, and conveys the heat liberated to the refrigerating water. The cock, D, regulates the reflux to the evaporator, A.

As an instance may be taken Pictet's machine (Fig. 229), which uses a mixture of sulphurous acid and carbonic acid, as is alleged, in the molecular combination, CSO_4.

Fig. 228.

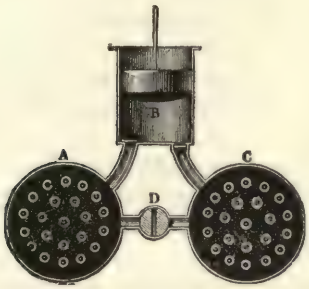
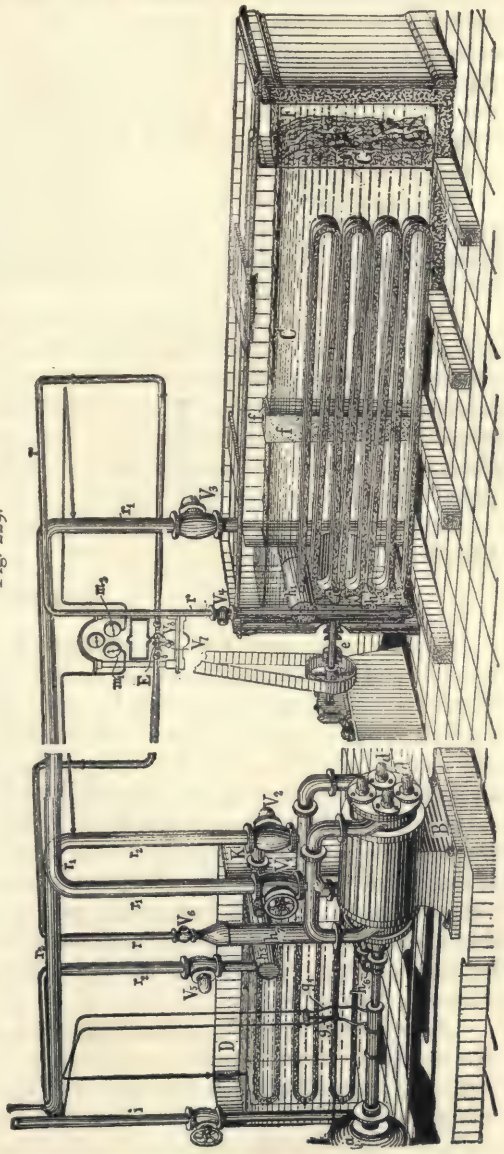


Fig. 229.



The cylinder, *a*, of the steam-engine, drives directly the forcing-pump. On each of its covers there are two suction-valves and two pressure-valves, *d*. The valves on both sides are connected with each other by a pipe. Above each of these two connecting-tubes there is a valve, V_1V_2, which can be shut perfectly air-tight. The water for the cooling-jacket of the pressure-cylinder and the perforated piston-rod arrives and is carried off by flexible tubes, *g*. The refrigerator, C, consists of two iron holders, and the worms. The former are set in each other so that they have one side on the bottom in common. The seamless worms of iron, or copper, all run above and below each into a large horizontal main, h_1 and h_2, which are again connected by two vertical tubes, h_3 and h_4. The liquid coming from the condenser is led below into the refrigerator by the tube, *r*, fills the lower horizontal tube, a part of the vertical, and of the worm, and is again drawn off in a gaseous form through the tube, *r*, by means of the forcing-pump. The valve V_3 and the entrance cock, V_4, allow of the whole system being closed air-tight.

The salt water flowing round the latter is kept in motion by the screw, *e*. This salt water, which is cooled down by the development of cold which proceeds in the worms, is conveyed by special conductors into the fermenting and storage cellars (*i.e.*, supposing the machine is in use in a brewery), and returns to the refrigerator,

heated several degrees. Iron cells, *f*, can be suspended between the worms, in which water is allowed to freeze. In the space between the two holders there is pure water, F, which covers the outer surface of the internal holder partly in the form of ice, G. This cold pure water serves to circulate in the beer coolers and fermenting vats.

The condenser, D, likewise consists of an iron receiver and a system of worms. The parallel worms discharge above and below into upright collecting tubes, h_5 and h_6. The compressed gases enter the condenser through the pipe, r_2, and are liquefied. The liquid collects at the bottom of the tube, h_7, and rises up through a narrower tube, *r*, which extends to the bottom of this large pipe. This pipe conveys the liquid through the regulator, E, to the cooler. The condensing worms are closed perfectly air-tight by the valve V_5 and the cock V_6. The cooling-water enters the condenser below through a pipe, *i*, traverses all the rows of worms, and flows off at the top through a perforated collecting-tube, *K*.

The regulator is introduced into the tube, which leads the volatile liquid from the condenser to the cooler after it has been liquefied. The bye-cocks, V_7 and V_8, attached to the main cock, allow the liquid to be introduced into the apparatus and to draw it out of the machine.

The latent boiling-heat of the liquids concerned is per kilo.: ammonia, 315; methyl-ether, 130; sulphurous acid, 94; ethyl-ether, 90; carbonic acid, 84 heat-units (calories). On account of the different specific heats and densities, the proportionate sizes of the machines are as follows: That of the ammonia-machine (according to Linde) = 1; ethyl-ether, 12·2; sulphurous acid, 2·5; methyl-ether 1·5; carbonic acid, 0·17. Theoretically, therefore, carbonic acid is the most advantageous. Trustworthy comparative experiments are still wanting.

Cold-air machines are to be preferred only where rooms have to be cooled and ventilated at the same time.

SULPHUR.

Sulphur occurs native in gypsum and in the connected beds of clay and marl, in the flötz and the tertiary formation, more rarely in veins in the crystalline slate and transition formations, occasionally in lignite and coal. It is also found as a sublimation product from volcanoes, as in the Solfatarae of Naples. It is most common in veins and deposits in Sicily, which supplies nearly all Europe with sulphur; in the Caucasus; in Egypt, on the coasts of the Red Sea, and especially of the Gulf of Suez; in the Ionian Islands (especially Corfu), in the Clear or Borax Lake in Nevada; in Popocatepetl in the Mexican province of Puebla, where above 100 tons of sulphur are collected yearly, and at Krisuvik in Iceland. Sulphur is plentifully found at Swoscowice near Cracow, deposited in the marl. It occurs also on a large scale in New South Wales. Sulphur is deposited from mineral springs, and occurs in combination with metals, as iron, and copper pyrites, galena, blende, &c., also oxidised to sulphuric acid in anhydrite, gypsum, kieserite, heavy-spar, &c.

Extraction.—Volcanic sulphur is obtained, according to the nature and the richness of the minerals—either by fusion or distillation. If the raw materials are rich the sulphur is extracted by melting in an iron pan, *A* (Fig. 230), which is gently heated by a fire on the grate, *B*. After the sulphur is melted the stony matter is skimmed out with the ladle, *C*, and the sulphur is poured into a dish moistened with water or into a sheet iron pan, *D*. When cold the mass of sulphur is broken up and packed in casks for the market. The stony matter, as well as the poorer sulphur minerals, are melted in heaps or shaft furnaces (Fig. 231), a part of the sulphur serving as fuel. A small quantity of impure sulphur is burnt in the support of this furnace, and the shaft, *E*, is gradually filled with coarse pieces of the earthy sulphur, which soon take fire on the top and allow the melting sulphur to escape. The openings, *f*, let in the air necessary

for the combustion of a part of the sulphur. The melted sulphur which collects at the lower part of the shaft is let off through the channel, *g*, into wooden or iron vessels. Sulphur can be melted in clamps better than in shaft furnaces. There are no fewer than 630 sulphur mines at present in work in Italy. In many the operation is effected in the most primitive manner by melting out a part of the sulphur by means of burning sulphur. This is effected in Sicily with an average loss of 50 per cent. of the total sulphur, and in the Romagna with a loss of 43 per cent. Other methods of extraction have only met with a very limited adoption.

Fig. 230.

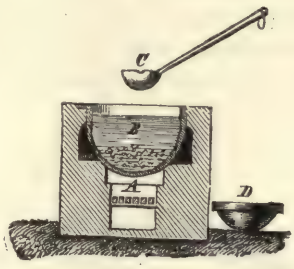
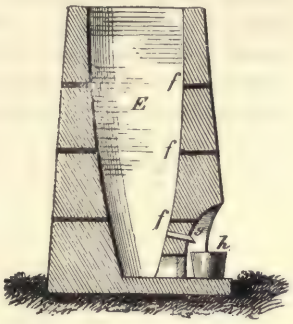
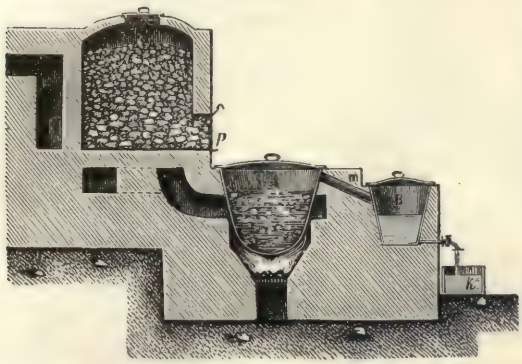


Fig. 231.



Far better is the distillation process, in which a real distillatory apparatus is now used (Fig. 232). A cast iron-pan, *A*, is filled with the raw material and closed with an iron cover. The manner of heating and the way which the products of combustion take round the pan and the preliminary heater, *D*, can be perceived from the figure. The vapours of sulphur escape through the iron pipe, *m*, into the condenser, *B*, from which the liquid sulphur runs into the vessel, *k*. The material, which has been previously warmed in *D*, is let fall into the pan of the still (which has been emptied in the meantime) by withdrawing a slide at *p*.

Fig. 232.



For extracting the sulphur from Italian ores, Balard recommended in 1867 a solution of salt. Dubreuil used a solution of calcium chloride, a procedure which had been carried out practically by Ch. Depérais in 1868. For some years sulphur has been eliquated from its ores by means of steam, at 130°. According to Gerlach's proposal, which has not been successful, the sulphur ores are heated with the simultaneous introduction of superheated steam. The extraction of the mineral with carbon disulphide has also found a restricted application.

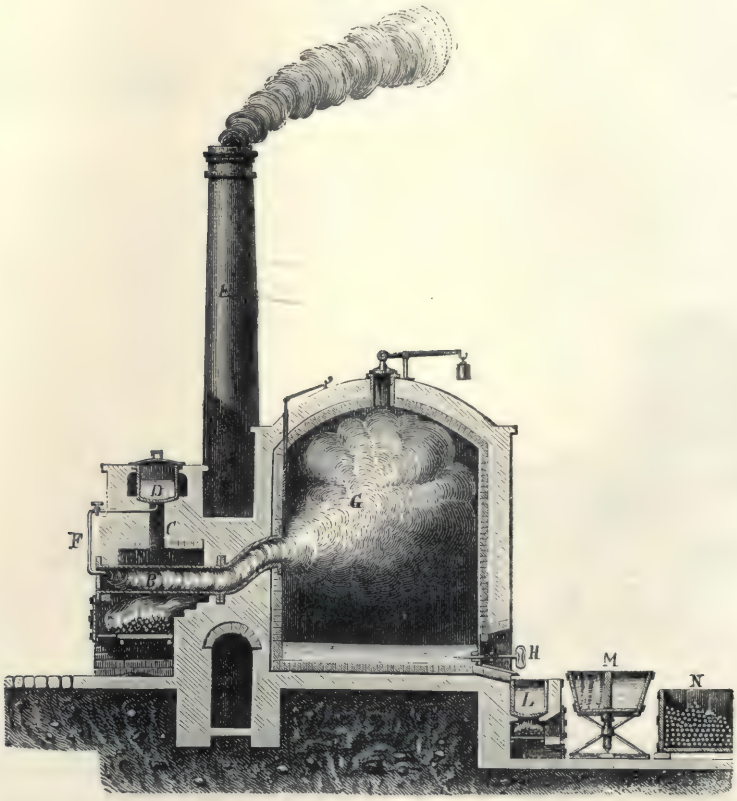
The Sicilian raw sulphur, as obtained by the fusion-process, had the following composition:

	I.	II.	III.	IV.	V.
Sulphur, soluble in CS_2	90·1	96·2	91·3	90·0	88·7
Carbonaceous matter	1·0	0·5	0·7	1·1	1·0
Sulphur insoluble in CS_2	2·0	—	1·5	2·1	1·7
Sand	2·3	1·5	3·3	2·8	5·5
Limestone	4·1	1·8	2·5	3·0	2·8
Loss	0·5	—	0·7	1·0	0·3

Refining.—The bottoms of the loaves of raw sulphur contain as much as 25 per cent. of foreign matter. In order to free it from the earthy parts the crude sulphur is refined and comes into the market either as roll sulphur or as flowers of sulphur.

The apparatus for refining sulphur, constructed by Michel, of Marseilles, and improved by Lamy, consists of one or of two cast-iron cylinders, *B* (Fig. 233), which serve instead of a retort, and a large chamber, *G*, which acts as a receiver. The first cylinder, *B*, is heated by the fire below. The flame plays round the cylinder and escapes, along with the gases of combustion, through the chimney, *E*, after having first given off a part of their heat to the pan, *D*, through the flues, *C*. Here the sulphur undergoes a preliminary purification and flows through the pipe, *F*, into the cylinder, *B*, which opens into the large vaulted chamber of brick. At one end of this chamber (not shown in the figure) there is a doorway closed inwardly by an iron door coated with lead and secured without by bricks. At the lower part of the chamber there is, in an iron plate, a round hole which can be opened or closed by the rod, *H*. The

Fig. 233.



sulphur flows from here into the pan, *L*, near which is a rotating vat, *M*, divided into compartments, into which the sulphur passes in the form of rolls, and is then stored in *N*.

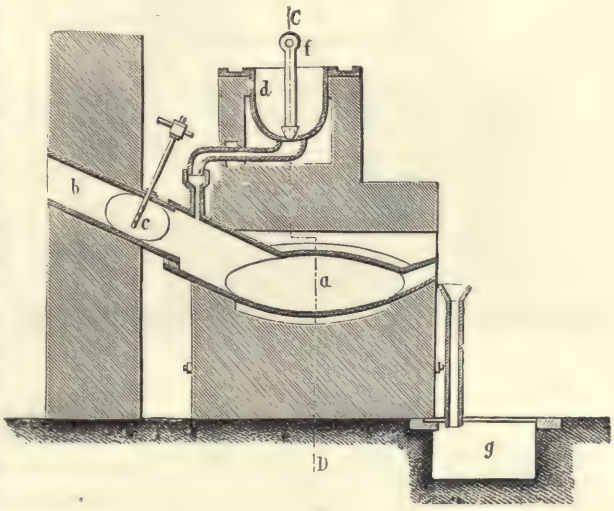
If roll sulphur is to be produced, each cylinder is charged with raw sulphur, the covers are luted and one cylinder is heated; as soon as the distillation is half effected the second cylinder is heated. The combustion gases from both hearths raise the temperature of the pan, *D*, so far that the sulphur melts and is thus purified, by the subsidence of the heavy impurities, by the escape of the moisture present, and by the separation of light matters on the top. As soon as the distillation of the first cylinder is at an end it is charged afresh from the pan, *D*, by means of the pipe, *F*. Each distillation lasts four hours, and 1800 kilos. of sulphur are obtained in twenty-four hours from the two cylinders in six operations. As the temperature in the chamber is always

above 112°, the sulphur remains liquid. As soon as the stratum of melted sulphur is deep enough it is drawn off into the small pan, *L*, and ladled into wooden moulds.

If flowers of sulphur are to be produced, the temperature in the chamber must not exceed 110°, as the sulphur would otherwise melt; to keep down the heat, only two distillations of 150 kilos. are undertaken in twenty-four hours. As soon as the layer of flowers of sulphur at the bottom of the chamber has reached a certain height the door above mentioned is opened and the flowers of sulphur are shovelled out.

In Dujardin's refining apparatus the distillation is effected in a lenticular retort, *a* (Figs. 234, 235, 236), with an annex, *b*, capable of being closed by the trap, *c*, in order that no air may enter while the retort is emptied. On the hearth is an oval pan, *d*, heated by the escaping fire and connected with the retort by the tube, *e*, which can be closed by the plug, *f*. This pan holds 600 kilos. of sulphur, which, as soon as melted, is let run with all its impurities into the retort. When it is volatilised (in about four hours) the trap is closed and the residue is emptied into *g*. In general, six distillations are completed in twenty-four hours, using 500 kilos. of fuel. In about five or six days the sulphur is cast into rolls. Only 400 kilos. of raw sulphur are daily distilled for the production of flowers of sulphur. The experience of the Wyndt-Aerts works at Merxem, near Antwerp, where such a furnace is in action, shows that the total loss does not exceed 2·23 per cent. and that the residues are quite free from sulphur. This is effected with crude sulphur which contains on the average 1·5 per cent. of impurities, so that the true loss is reduced to 0·73 per cent. In the works in which this apparatus is in action 1500 tons of sulphur are distilled yearly.

Fig. 234.



Still simpler than the above Belgian apparatus is one used in German refineries, consisting of two cast-iron pans of 1 metre diameter and height, at the distance of 2 metres from each other and connected with each other by a knee-piece. The one pan is fixed over a grate fire and is charged by means of a funnel going down through the knee-piece and descending almost into the melted sulphur, whilst the refuse is removed by a side-tube. The vapours of sulphur as they are driven over condense in the second pan which is bricked round so that the melted sulphur may remain liquid and may be let off by a cock.

Commercial flower of sulphur always contains sulphurous and sulphuric acids, which may be chiefly removed by washing with water.

Sulphur from Iron Pyrites (Sulphur Ores), FeS_2.—Iron pyrites may give off 26·65 parts of sulphur without being rendered unfit for the manufacture of copperas (ferrous sulphate). But if half the sulphur present in the pyrites were to be expelled by heat it would be necessary to apply a temperature at which the residual iron monosulphide would fuse, and would be absorbed into the fire-clay cylinders and destroy them. It is therefore thought preferable to expel only 13–14 per cent. sulphur by heat when the residue remains pulverulent and does not attack the distillatory vessels. Iron pyrites

always contains arsenic. According to the analyses of E. Hjelt (1877) Spanish pyrites contain 0·91 per cent.; Westphalian 0·3; Norwegian only traces.

The pyrites are heated in conical tubes of fire-clay, *A*, which, as shown in Fig. 237, are laid over a fire in an inclined position. The lower opening is closed with a sieve-plate of burnt clay, *A*, which prevents the pyrites from falling out, but allows the melted sulphur to escape either as a liquid or as a vapour. At this end there is an earthen tube, *b*, through which the sulphur arrives in receiver, *C*, containing water. The tubes are filled with coarsely pulverised pyrites, closed with fire-clay lids luted on and then heated. The raw sulphur found in the receiver is of a greenish-grey colour and is purified by re-melting. Such sulphur is met with in commerce in lumps as melted sulphur. In order to purify it from the accompanying arsenic sulphide it is redistilled. The residue from this is the so-called horse-sulphur used in veterinary practice. The orange colour of the sulphur obtained from pyrites is owing more frequently to an admixture of thallium than to arsenic. Crookes found in Spanish pyrites-sulphur as much as 0·29 per cent. of thallium.

Fig. 235.

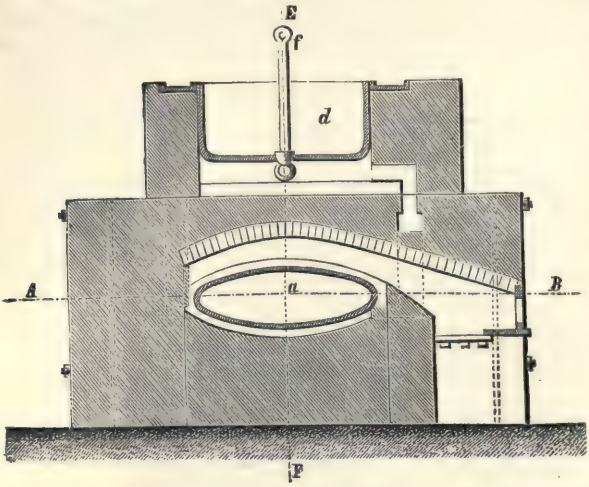
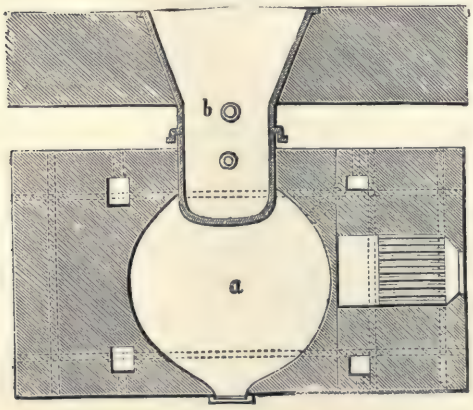


Fig. 236.



Section across *A B*.

Sulphur from Roasting Copper Ores, as a bye-product of the extraction of copper.—In the Lower Harz so-called virgin sulphur was formerly obtained in stalactitic pieces from copper pyrites, the sulphur being let drop out at an opening in the side of the roasting-heap.

Gas-Sulphur, as a bye-product at gas-works.—In purifying gas with Laming's mass the sulphur collects in quantities up to 40 per cent. according to the equation: $Fe_2O_3 + H_2S = 2FeO + H_2O + S$. The sulphur is extracted with carbon disulphide, or the mass is roasted in kilns for the manufacture of sulphuric acid.

Sulphur from Vat Waste.—See Alkali Manufacture.

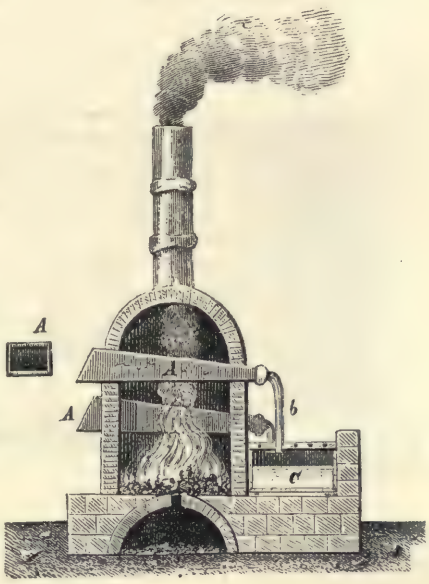
Sulphur from Sulphurous Acid and Sulphuretted Hydrogen.—Dumas in 1830 observed that if $\frac{1}{3}$ sulphuretted hydrogen is burnt and the sulphur dioxide produced is passed into a moist chamber along with $\frac{2}{3}$ sulphuretted hydrogen, almost all the sulphur might be recovered: $SO_2 + 2H_2S = 2H_2O + 3S$. This reaction, in which nearly half the sulphur is lost by the formation of pentathionic acid, has been often tried in order to recover the sulphur from gypsum, cœlestine, heavy spar, and the residues of the Leblanc alkali process (according to the method of Schaffner and Helbig). The process is essentially as follows:—Heavy spar, *e.g.*, is reduced by ignition with carbon to barium sulphide,

which is then heated with hydrochloric acid or magnesium chloride in order to obtain on the one hand barium chloride and on the other sulphuretted hydrogen, which is either partially burnt and then converted into sulphur by means of the unburnt sulphuretted hydrogen according to the above reaction, or the sulphuretted hydrogen gas is at once passed into water or a solution of magnesium chloride into which there is passed at the same time sulphur dioxide produced by roasting pyrites. By a similar reaction sulphur is also obtained as an important bye-product in the extraction of potassium salts and iodine from kelp. At Paterson's iodine-works in Glasgow the annual yield of sulphur from kelp is about 100 tons. According to C. Kopp sulphur may be also obtained by the imperfect combustion of sulphuretted hydrogen ($H_2S + O = H_2O + S$).

Sulphur from Sulphurous Acid and Carbon.—If sulphurous acid is passed over ignited coals the latter burn to carbon dioxide, and sulphur is eliminated. In this manner sulphur is obtained at Borbeck on roasting zinc blende.

Sulphur from Sulphuretted Hydrogen.—Sulphuretted hydrogen if passed through tubes at a red-heat is resolved into its constituents. It is passed through ferric hydroxide suspended in water, when the gas is entirely absorbed. The iron sulphide is converted into free sulphur and ferric hydroxide if air is forced in.

Fig. 237.



Properties. — In its ordinary condition sulphur has a peculiar yellowish colour, which becomes darker at 100° and almost disappears at 50°; it is easy to pulverise; its spec. gr. is 1·98–2·06; it melts at 113°–113·5° to a thin yellow liquid, which becomes thicker and of an orange-colour at 160°; at 220° it becomes tough and reddish; between 240° and 260°, very tough and reddish-brown; at 340° it grows more liquid again; and at 448·4° (Regnault), without losing its dark colour, it begins to boil and is converted into dark reddish-brown vapours. If sulphur is heated to 230° and is suddenly cooled by plunging into water, it becomes soft and plastic, and in this state it can be used for taking impressions of medals and other engraved work. After some days it recovers its original hardness, so that the impressions can be used as moulds for reproducing very sharp copies. If sulphur is heated in contact with air it burns to sulphurous acid. It is insoluble in water, very slightly soluble in absolute alcohol and ether, more readily in carbon disulphide, 100 parts of which at 48·5° dissolve 146·21 parts of sulphur. It is also soluble in heated oils, fatty and volatile, and dissolves on boiling in soda and potassa-lye. It is used in the manufactures of gunpowder and matches, for sulphuring hops and wines, for applying to trees as a remedy for the parasitic diseases, for the preparation of sulphurous acid, sulphites and thiosulphites, carbon disulphide, vermilion, mosaic gold, and other metallic sulphides, in the manufacture of certain cements, and for vulcanising caoutchouc and gutta-percha.

Besides Italy, with about 400,000 tons, Spain yields yearly 6000 tons, Austria and Germany each 900 tons (not including regenerated sulphur), and the rest of Europe 900 tons of sulphur.

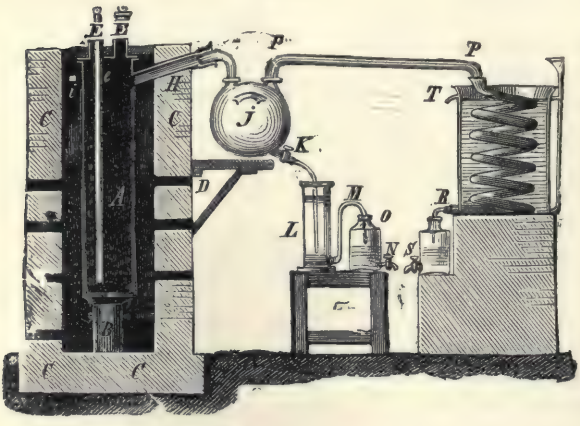
Carbon Disulphide, CS_2.—This compound (which was discovered by Lampadius in 1796) is obtained by bringing sulphur in contact with ignited carbon, or distilling

metallic sulphides (pyrites, blende, &c.) with carbon. The yield, according to W. Stein, is best when the vapour of sulphur is allowed to act upon carbon at a medium grade of redness.

In the manufacture of carbon disulphide the apparatus of Peroncell is often used (Fig. 238). A clay gas-retort, *A*, stands on a stone support, *B*, and is built into a furnace. On the cover of the cylinder there are two necks, *E*, into one of which is cemented a porcelain tube which extends almost to the bottom of the cylinder and rests upon a layer of pieces of charcoal with which the bottom is covered and with which it is otherwise filled up. The sulphur is added through this opening, *E*, fitted with the porcelain tube, and through the other opening charcoal is added from time to time. The fumes of carbon disulphide formed escape through the lateral tube, *H*, into the stoneware receiver, *J*, in which a part of the carbon disulphide is condensed and flows through *K* into the Florentine flask, *L*, and thence through the bent tube, *M*, into the jar, *O*, from which it can be let off by means of the cock, *N*. The vapours not liquefied in *J* pass through the pipe, *P*, into the cooling-apparatus, *T*, from which it escapes at *R* into the receiver, *S*.

Notwithstanding the most careful refrigeration, the quantity of disulphide is never obtained which the weight of sulphur employed should theoretically yield, not only in consequence of the unavoidable loss of a part of the carbon disulphide, but probably from the simultaneous formation of carbon monosulphide (CS, corresponding to carbon monoxide), which is formed to some extent along with the disulphide. The product obtained contains 10 to 12 per cent. sulphur in solution, in addition to sulphuretted hydrogen and, doubtless, some other compounds of carbon, sulphur, and oxygen, which give it an exceedingly unpleasant smell. It is purified by rectification, solution of chloride of lime being introduced into the apparatus, which destroys the sulphuretted hydrogen, and the rectification is then begun by passing steam at one atmosphere underneath the still. According to Braun, pure carbon disulphide may be obtained by repeated distillation over a pure fatty oil. In order to protect carbon disulphide in the refrigerators, &c., from evaporation, it is kept covered with a layer of water of 20 to 30 centimetres in depth.

Fig. 238.



Properties.—When pure, carbon disulphide is a limpid, colourless, motile liquid which refracts light strongly and has an odour somewhat like that of chloroform, and an aromatic flavour. Its spec. gr. = 1·2684. It boils at 46·5° and evaporates quickly at common temperatures. Its ignition point is 170°. It does not combine with water, but mixes with it in the proportion of 1 per cent. It is miscible in all proportions with alcohol, ether, and similar liquids. It dissolves resin, fatty and ethereal oils, caoutchouc, gutta-percha, wax, camphor, sulphur, phosphorus, and iodine, in large quantity. It is very readily inflammable, and burns with a faint blue flame to form sulphurous and carbonic acids (whence its utility in extinguishing burning chimneys and fires in close spaces, such as cellars and magazines). A mixture of its vapour with oxygen or atmospheric air gives a violently explosive gas. A mixture of nitric oxide and vapours

of carbon disulphide give, when ignited, a very intense light, which has been used in photography.

Up to 1850 the only use of carbon disulphide on the large scale was in vulcanising and dissolving caoutchouc. Latterly it has been employed for extracting fat out of bones which are to be used for the preparation of animal charcoal; for extracting oils from oil-seeds (palm kernels, olives, rape-seed, linseed, poppy-seed, &c.), for extracting sulphur out of minerals, asphalt from bituminous rock, and recovering oil and fat from matter in which it was formerly lost (such as the "glycerine tar," the *glycerine goudroneuse* of the French stearine works, where it is found as a bye-product of the saponification with sulphuric acid), from the brown residues of wheel-grease, from saw-dust which has served for filtering oils which have been refined with sulphuric acid; from the dregs of tallow-melting, the so-called greaves; for extracting fat from wool and waste used in cleansing machinery—the fat thus recovered may be used in soap-boiling; in the production of potassium ferrocyanide on the Tcherniak and Güntzburg process and of ammonium sulphocyanide; for purifying raw paraffine by Alcan's process; in electro-plating—a small quantity of carbon disulphide is added to the silver bath to give at once a brilliant surface; for killing rats and other vermin; a solution of wax in carbon disulphide is used in preparing wax paper and in coating plaster figures. König burns carbon disulphide in an especial lamp for disinfecting, and Dahlen uses it for sulphuring casks. Recently, compounds of the alkali-metals with sulphocarbonic acid, $CH_2S_3 = CS(SH_2)_2$, have been successfully used in a watery solution as a remedy for the phylloxera. The salts of xanthogenic acid (ethyl disulphocarbonic acid), a derivative of carbon disulphide, have been used by Zöller for preserving articles of food, and by H. Schwarz for producing explosive mixtures. The vapour of carbon disulphide is recommended against the grape-disease.

Sulphur Chloride (Cl_2S_2) is a compound used for vulcanising caoutchouc. It is an oily liquid of sp. gr. 1·60; is of a brownish colour and has a suffocating smell; it fumes in the air and boils at 144°. In contact with water it is quickly decomposed into sulphurous and hydrochloric acids, sulphuric acid, and sulphur. Sulphur chloride is a good solvent for sulphur; it converts rape oil into a mass resembling caoutchouc, and linseed oil into a varnish. It is obtained by passing chlorine gas, washed and dried, through melted sulphur heated to 125° to 130°. Sulphur chloride is at once formed, and distills over into a cooled receiver, carrying with it vapours of sulphur. It is redistilled to purify it from free sulphur.

Sulphurous and Sulphuric Acids.—Sulphurous acid, SO_2 (more correctly named sulphur dioxide), is obtained by the combustion of sulphur, by roasting metallic sulphides, or by the reduction of sulphuric acid.

The furnaces, kilns, or burners are built of bricks (Fig. 239); at a height of 80 centimetres above the floor there is placed a stout iron plate, sloping slightly forwards. Upon this plate rest the side-walls, whilst the back and the top of the furnace are also formed of iron plates. The same applies to the front side of the furnace, in which there are several (three to six) large openings, *P*, which are closed with iron plates fitted with wooden handles. Within, upon the iron plate which forms the sole of the furnace, there are three iron rails, placed lengthwise, each 10 centimetres in height, which divide the bottom into three or six compartments, corresponding to the number of the doors. At *H*, there are air-holes. From the iron plate which forms the top of the furnace there goes off a wide pipe, *T*, which carries off the gases and vapours formed in the furnace. In starting this furnace the workman places about 50 kilos. of lump sulphur in each compartment, and kindles the surface; the draught through the air-holes, *H*, is regulated so that the required quantity of sulphur burns to sulphuric acid, but that no sulphur sublimes. If the furnace is at the same time to furnish the nitrous vapours necessary for the formation of sulphuric acid, there is introduced into each compartment a

movable furnace on feet, in which is a mixture of soda-saltpetre and sulphuric acid at 116° Tw. (= 1·56 spec. gr.). The combustion heat of the sulphur causes hyponitrous acid to be evolved from this mixture, which escapes along with the sulphurous acid through the pipe, *T*.

Fig. 239.



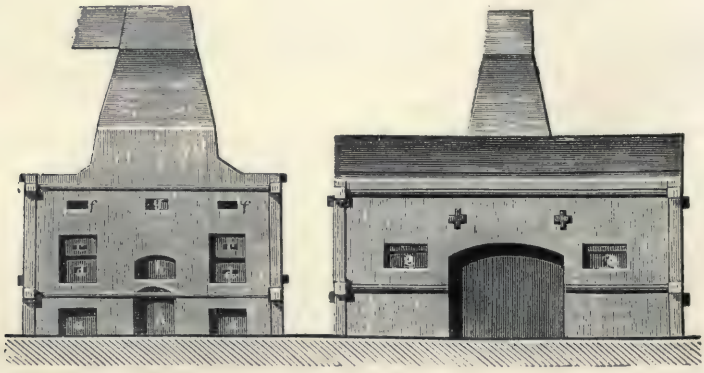
However much these furnaces have been improved, they labour under the defect that in them the sulphurous acid is not evolved continuously, but in fits, by which the regularity of the process is endangered. It is better to use sulphur furnaces with an uninterrupted working, in which an equal current of melted sulphur flows down upon the burner-plate, and forms in every part of time the same quantity of sulphurous acid.

To every square metre of the floor of the furnace 60 to 70 kilos. of sulphur are allowed in twenty-four hours, and to every 100 cubic metres of the lead chambers 46 to 50 kilos. of sulphur in small works, in larger ones 66 to 100. The sulphur ovens are being gradually superseded by those for pyrites or blende.

The furnaces for roasting pyrites consisted at first of a shaft without a grate. In the vault there were two openings, the one connected with the chimney and the other with the lead chambers. In the front and the back there were a number of holes which served to admit air and to watch the process. The upper aperture was for the introduction of pyrites, broken to the size of a nut; the lower was for the removal of burnt ore.

In the Oker works, in the Harz, similar kilns are in use, according to W. Knocke. For every four kilns there are two nitre-channels, which lie so between the furnace-shafts that the temperature is reached which is needed for decomposition. Figs. 240,

Fig. 240. Fig. 241.



241, 242, 243, give a front and side elevation and the corresponding sections. Two rows of two or four kilns each are in contact with the back wall. *a* and *b* are openings for drawing out the burnt ore; *f*, openings for introducing the charge (a mixture of 80 per cent. iron pyrites and 20 per cent. copper pyrites) containing about 50 per cent. sulphur; *c*, *d*, *e*, *i*, are openings for stirring up the ore and keeping up the current of air; *g*, are the nitre-channels. In the space, *h*, cast-iron nitre boxes are kept ready filled. In twenty-four hours 2700 kilos. of ore are roasted, and 50 kilos. nitre are consumed.

When the kilns are new they are heated for some days by a wood fire placed on

the sole of the furnace and gradually strengthened; roasted ore is then introduced up to 10 centimetres below the door, and upon this ore there is kept up a strong flame fire until the sides of the kiln, and especially the vault, are red hot. Raw ore, in pieces from the size of a walnut to that of a fist, is placed upon the roasted ore to the depth of 9 to 12 centimetres. The raw ore is ignited by the heat of the kiln and the wood fire, and is roasted. The vapours are passed into the open air as long as the wood fire is in existence. When it is consumed and the ore is in full glow, the vapours are conveyed into the chambers. The workmen continue in this manner drawing out as much burnt ore below as they put in raw ore above. The kilns are worked so that each is emptied and refilled three times in twenty-four hours, and attended to three times. Every two hours two kilns are charged afresh and two others are attended to. The attention

Fig. 242.

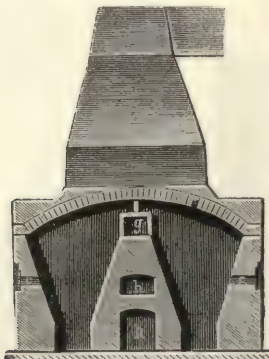
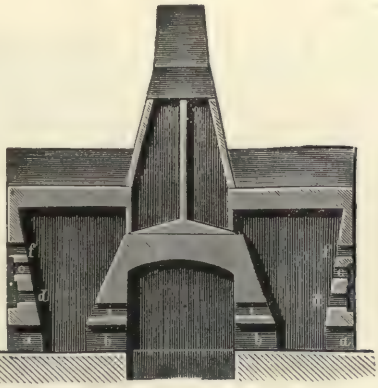


Fig. 243.



takes place four hours after charging, and consists in breaking up the ore with iron bars, that the air may have proper access. The air required for the oxidation of the sulphur enters chiefly from below, through the roasted ore. If there is any deficiency it is made up by admitting air at the slides in the side doors. The soda-saltpetre is placed in cast-iron boxes, with sulphuric acid, at 30° Tw., and placed in the channels. In the course of four hours they are replaced by fresh nitre boxes, so that each channel is freshly supplied six times in twenty-four hours. In roasting, care must be taken that the fire does not work downwards and so smelt the mass together. The ore must not be placed too closely together, or be broken up too finely.

Fig. 244.

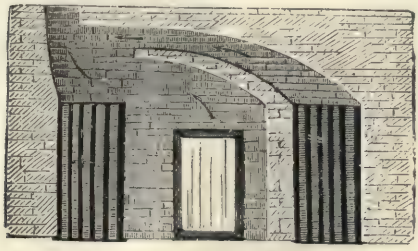
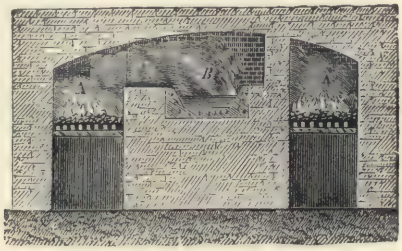


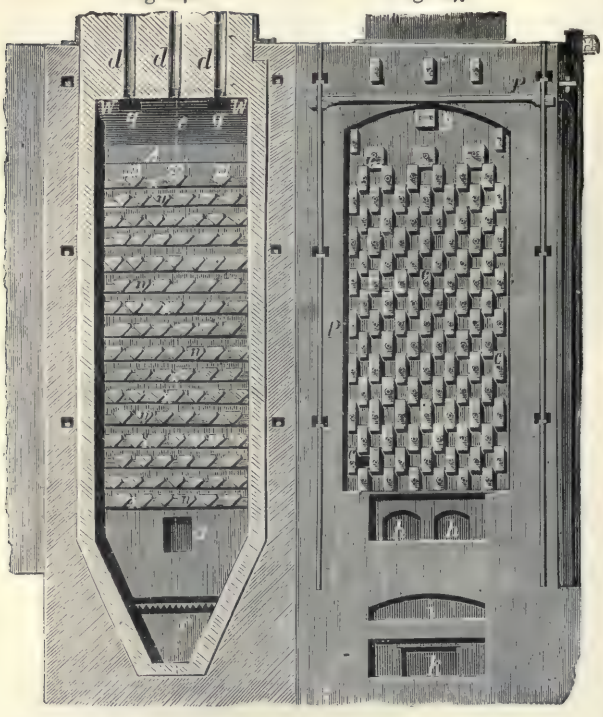
Fig. 245.



In the sulphuric acid works at Marseilles pyrite kilns with grates are used, arranged as shown in Figs. 244 and 245. They consist of two hearths, *A*, with grates. Between them is a pan of sandstone or cast-iron for the mixture of nitre and sulphuric acid. The gas of the one hearth, separated by a tongue from the other, that the nitre pan may not be over-heated, meets with the other gases shortly before the exit from the kiln. Slits in the doors admit the air. Each hearth is charged with 150 kilos. of pyrites broken so as to pass a 2-inch sieve. A furnace with two hearths roasts 2000 kilos. pyrites in twenty-four hours.

In the Gerstenhöfer roasting kilns (terrace kilns) the comminuted ore falls through hoppers fitted with grooved rollers upon earthen bearers, and slips down from one stage to another, being kindled by the ignited sides of the furnace which have been previously heated by fire upon a removable grate, and roasted by the action of the air admitted at the sides. The burnt ore which falls upon the sole of the furnace (which narrows below) is drawn out at a side door. In the roasting space, *A* (Figs. 246 and 247), there are, besides the three upper distributors of the ore, *m*, fifteen rows of ore-bearers, *n*, each alternately of six and seven pieces of Meissen clay (together 100 in number); the bearers with corresponding sections come in contact with projections of the stones in the front and back walls. The roasting-gases from *A* arrive through the space, *e* (Fig. 248), into the flue-dust chambers, *C* and *E*, and thence into the lead-chambers. In a vaulted passage, *D*, through the flue-dust chambers, *E*, are the valves in the air-chest, by means of which is regulated the access of air into the furnace through the channel, *l*, and the opening, *a* (Figs. 246 and 247). The flue-dust settling in *B* can be removed through openings, *q*, in the vault. For introducing the ores through the slits, *d*, the three distributors there serve the shoot-arrangement above. On the platform of the furnace stands a cast-iron chest on feet, 9 centimetres broad; its right and left sides are straight, but its front and back are bent in. After it has been set in its place, the masonry of fire-bricks is carried up within the sides as far as 9 centimetres below its upper angle, keeping the space for the slits open, and the angle formed on the right of each slit is kept so broken off that a curved cast-iron plate, which conveys the ore to the rollers, is supported both by the wall and on the projections of the chest. To protect the roller-bed from direct contact with the fine mass of the charge, two cast-iron plates are laid over each, resting partly in a niche left in the masonry and partly upon a three-sided prism-shaped piece laid upon the plate. The covers of the slits have two handles; they prevent the direct fall of the charge into the slits, and cause it to enter the roasting shaft only between the rollers and the guiding plate, thus rendering it possible for it to be introduced always in equal quantity and not beyond a certain limit. The two pieces screwed to the front wall of the chest support bearings for a shaft on which are fixed three endless screws which fit into the teeth of the wheels.

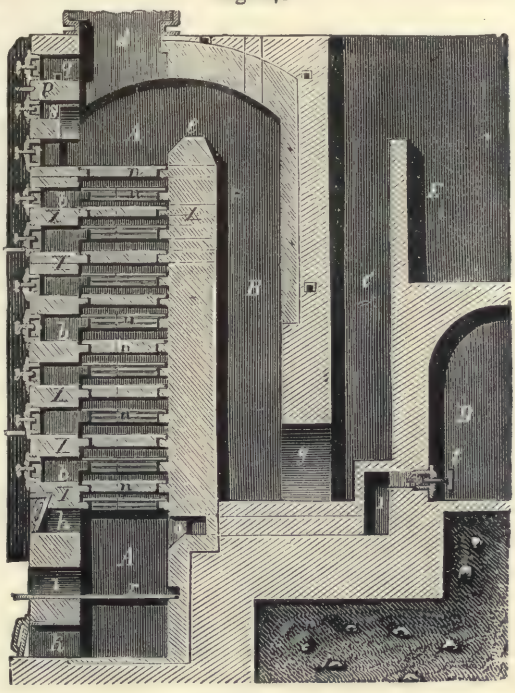
Fig. 246. Fig. 247.



For starting the furnace, fifteen or sixteen grate-bars, *r*, are inserted through the middle opening, *i*, which is then filled up with bricks and clay; the intervals between the grate-bars are filled up outwardly; coals are placed upon the grate through *h*, and kindled by a wood fire from below; the upper openings, *h*, are closed tightly with iron plates, but the exit hole, *k*, is left open. To prevent the ore-bearers from cracking, the furnace is heated to whiteness very gradually, the gaseous products, after the channel,

g, is closed, being passed, not into the lead-chambers, but through a side-flue into a chimney. The bearers are kept for two days at a white heat, and the rollers are then started, one turn in five minutes. The hoppers have been filled at the beginning of the heating, to prevent the combustion gases from escaping through the slits, *d*. By the movement of the rollers, the ore-bearers are gradually filled with the charge up to their natural slope, and the firing is continued, until it is observed through *c*, *b*, that about the fourth row of bearers from below is beginning to fill. One grate-bar after another is then drawn out, and the space is closed with bricks and mortar until the opening, *i*, is entirely blocked. The ash-pit is cleared out, and the valve, *m*, is opened to admit air through *a*. The filling with the charge at the above speed of the rollers takes about $6\frac{2}{3}$ hours. After the admission of air, the volatile products of roasting are still allowed for a while to escape by the chimney; afterwards the flue, *g*, is opened, and the one leading to the chimney is closed. As will be seen from the above description, the ore falls through the slits, *d*, at first upon the upper bearers, collects there as long as the slope allows, and then all further supplies of material slide down upon the next row of bearers. As to the uniformity of roasting, the Gerstenhöfer furnace is much superior to other shaft-furnaces, and especially to muffle-furnaces, as it contains an equal amount of the charge in all the horizontal sections at the same time. The ore must be supplied in a sufficiently fine form, that the roasting may be expeditious, and that the heat needed for keeping up the process may be supplied by the oxidation of the sulphur. If too much cold air is admitted, the heat moves upwards; if too little, it goes downwards. In the former case the furnace is too cold, and in the latter too hot. With normal working, almost a white heat is reached in the hottest part; if any irregularity appears, the air must be partly cut off or the rollers turned more quickly. The Gerstenhöfer kiln allows poor ores to be burnt without fuel, at the same time producing rich gas of uniform composition.

Fig. 248.



The Hasenclever and Helbig kiln renders it possible to burn smalls without an admixture of lump-ore. The ore is introduced through the hopper *a* (Fig. 249), and when roasted it is removed in proportion as fresh smalls slide down from the hoppers. The air entering the furnace passes upwards over the layers of ore on the lowest four or five plates, becomes heated and mixed with a little sulphurous acid, and leaves the furnace, rising upwards in a flue, becoming heated in contact with the gas-channels, enters the furnace above, and draws downwards when the hot gases leave the furnace in two shafts and enter the lead-chambers.

The plate-furnace of Malétra has come into extensive use on account of the simplicity of its construction, joined to the circumstance that it requires no fuel, and burns the ore very completely. This furnace is shown in longitudinal section in Fig. 250. Smalls are made to work down from plate to plate to meet the ascending current of

gases, and do not slide down spontaneously as in the kilns of Gerstenhöfer and Hasenclever-Helbig.

It is set in action by the grate, *a*, and the kiln-door, *b*, which are bricked up as soon as the furnace is in full heat. The plates, *a*, *b*, *c*, *d*, *e*, and *f*, are charged with smalls through the working doors, *h*, *i*, and *k*, when the ore at once takes fire. The furnace gases sweep, as the figure shows, over all the plates, pass through *m* into the flue-dust chamber, and through *o* to the lead-chambers. The ore is removed every two hours from one plate to the next. This furnace is especially adapted for smalls.

For roasting blende the furnace of Eichhorn and Liebig is suitable. It consists of a number of roasting chambers, *r* (Figs. 251 and 252), with six or more soles, perfectly separate from each other. They are heated from without by fire-gases drawn from a generator, *G*, and passing through the flues *n*. For the due distribution of the heat in the long flues the air of combustion, heated in the flues *l*, is conveyed to the generator-gases at three different places.

The blende has been previously heated on the top of the furnace by the radiant heat from the masonry, and arrives through the hopper *t*, on the highest sole of each separate roasting furnace, where it is uniformly spread out. After about six to eight hours it is brought down to the second sole, and after the same length of time to the third. This

Fig. 249.

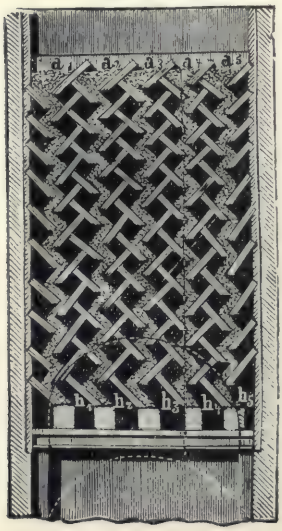
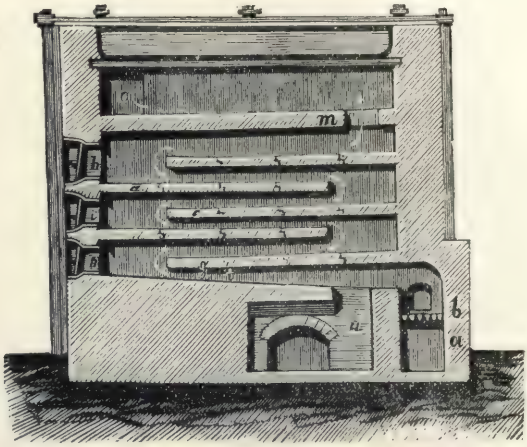


Fig. 250.



is effected through the breaks, *a*, in the bottom, which are alternately at the front and the back. Meantime, the upper sole is constantly charged with fresh ore through the hopper. The ore, according to its nature, remains from thirty-six to forty-eight hours in the furnace before it is completely roasted, and leaves the furnace through the vent, *k*, falling into the cooling space, *o*.

In order to obtain complete roasting on the sixth sole, the air which is admitted must be previously well warmed. For this purpose the openings into the furnace are closed as nearly air-tight as possible, so that the roasting air is compelled to take its way through a tube, *e*, placed under every roasting chamber; passing through small ducts left in the sole of the lowest flue (7), it is strongly heated. The access of the air for each chamber can be accurately regulated by a slide at the mouth of the tube, *e*. The heated air takes its way through the outfall channel, *k*, over the layers of ore—moving in the opposite direction—continually meeting charges richer and richer in sulphur, by the oxidation of which it becomes saturated with sulphurous acid, and finally arrives

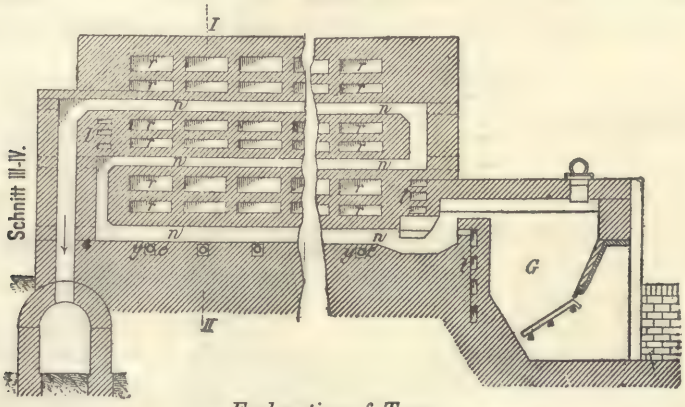
through the channel, *s*, at the flue-dust chamber, *V*, which is common to all the roasting-chambers, from which the roasting gases pass to their destination.

In such a furnace about 3 tons of blende are roasted in twenty-four hours; or about 333 kilos. per compartment. A charge is drawn every six hours from each compartment, and the blende remains thirty-six hours in the furnace. In the successive compartments the blende contains the following proportions of sulphur :—

Raw ore . .	31·2	...	31·2	...	31·2	...	31·2
Upper sole . .	28·0	...	23·8	...	24·3	...	24·2
Second sole .	24·8	...	22·7	...	19·7	...	21·5
Third sole . .	16·1	...	16·5	...	12·3	...	17·3
Fourth sole .	8·8	...	12·5	...	9·9	...	?
Fifth sole . .	7·8	...	7·8	...	5·4	...	5·6
Bottom sole .	0·96	...	0·9	...	1·29	...	1·33

At the Rhenania, near Aachen, the difficulty has been observed, according to Hasenclever, that the plates of these furnaces have to be often renewed. The mechanical

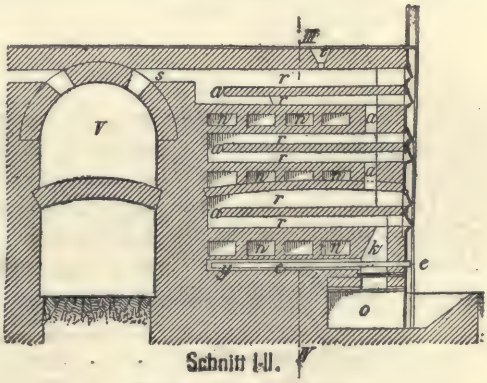
Fig. 251.



Explanation of Terms.
Schnitt III-IV—Section III–IV.

roasting-furnace of the Vieille Montagne Company is in action at the Rhenania and at Oberhausen.

Fig. 252.



Explanation of Terms.
Schnitt I–II—Section I–II.

This blende-furnace (Figs. 253 and 254) consists of several roasting-soles, *A*, one above another, to which there joins up a four-sided roasting-hearth, *B*. The broken ore shot into the hopper, *a*, is gradually moved downwards by means of two rollers, and the channels, *K*, to the upper roasting-sole, in order to be despatched to the lower roasting-plates by the revolving stirring-hooks. The fire-gases from *F* pass over the hearth, *B*, then through the roasting sides, *A*, and escape through the dust-chamber, *C*, into the exit channel *S*. The arrangement for stirring consists of an axle, *b*, passing vertically through the furnace with cross-rods, *e*, which carry the stirring-irons. The joint where this axle enters the furnace is packed with asbestos. The axle, *b*, is in an iron casing, *g*, to which it is secured in several places. In the interval between

g and *b* cold air ascends from below, thus preventing the too rapid destruction of the casing, *g*. The toothed stirring-irons, *m*, are fixed radially to the arms, *e*, and serve merely to stir up the ore. The smooth stirrers, *f*, on the other hand, are fixed obliquely to the radial direction of the arm, *e*, and according to the angle at which they are set, they move the ore either from the middle to the outside, or in the opposite direction. By means of an opening in the roasting-sole, which is introduced either in the middle or at the circumference, according to the position of the hooks, *f*, the ore, after being thus stirred up, passes down to the next lower floor, where it is again stirred up by the toothed irons, *m*, and removed by the smooth hooks, *f*, to the opening for the next lower sole. Lastly, the roasting is completed on the hearth, *B*.

The furnaces which have been recently introduced by the Rhenania at Stolberg consist of a series of muffles placed above each other and traversed by the fire-gases. The indirect heat suffices for the complete roasting of zinc blende. The ores are finely ground, placed upon the top of the furnace, filled upon the high sole by means of hoppers, and are thence removed by the workmen from muffle to muffle, and at the end of the lowest sole they are completely desulphurised. It requires frequent stirring. The air enters at the working-doors, and is converted into sulphurous acid

Fig. 253.

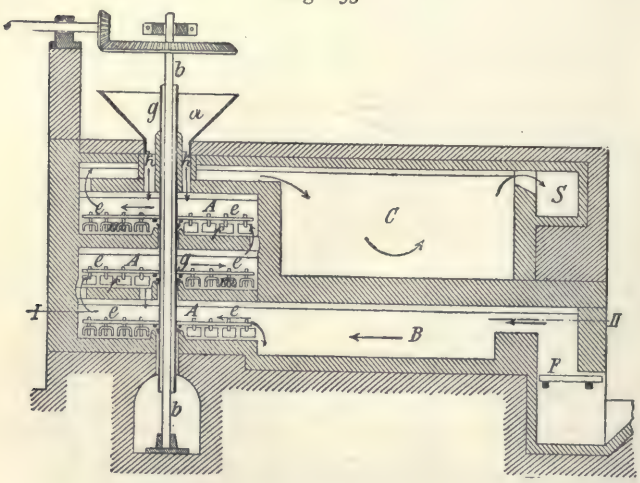
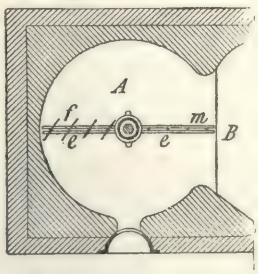


Fig. 254.
Schnitt. I-II.



Explanation of Terms.
Schnitt I–II—Section I–II.

in contact with the ignited ore. It is carried up in flues opposite to the working-doors and arrives in the lead-chambers. By means of these channels the escape of gas is not hindered, and it is possible to convey the products of a number of burners into the same lead-chamber, which is more difficult to effect when hot gases have to be conveyed horizontally.

In twenty-four hours the furnace, at which two men work in each twelve hours' shift, yields 3000 to 5000 kilos. of roasted blende. The consumption of fuel is at present 980 kilos. of Förd coals. The furnaces are worked partly with gas fires and partly with grates. The sulphur in the raw ore was :—

	19·2 per cent.		26·8 per cent.		26·5 per cent.
After 1st muffle . . .	17·6	...	19·1	...	15·4
,, 2nd ,, . . .	12·0	...	11·2	...	9·9
,, 3rd ,, . . .	3·4	...	1·02	...	0·75
Finished	0·6	...	0·35	...	0·75

The temperature varies according to the proportion of sulphur in the ores, and was in the first muffle 580° to 690° ; in the second and third 750° to 900°. In rich ores the middle muffle is hottest; in poor ores the highest temperature prevails below.

Pyrites contain almost universally small quantities of foreign matter, which interferes

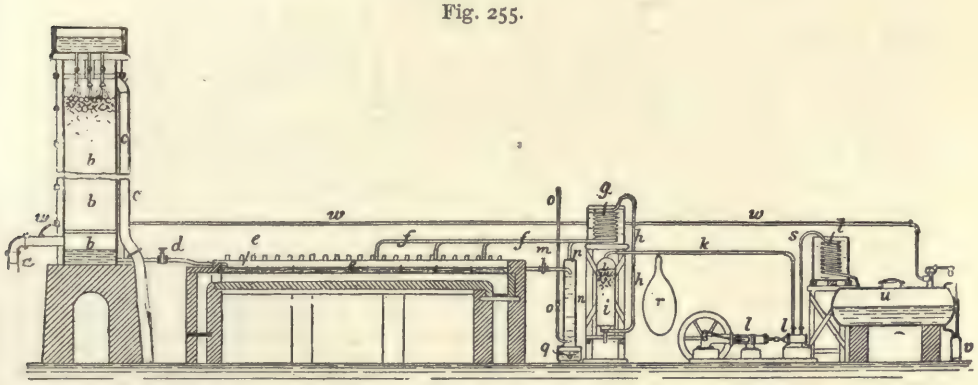
with the purity of the acid produced. Hence, in commerce, especially in England, a distinction is made between pyrites acid and brimstone acid, the latter being the dearer. It is known that the discovery of selenium is closely connected with the use of pyrites in sulphuric acid works; it was discovered by Berzelius in 1817 in the mud of the chambers of the works at Gripsholm, in Sweden, where pyrites from Fahlun were burnt for the production of sulphurous acid. In 1862 thallium was discovered by Crookes as accompanying selenium in the flue-dust of pyrites. When blende is burnt, the flue-dust may contain gallium. Tellurium is also found mingled with the roasted gases of certain pyrites. The arsenic of pyrites escapes on roasting as arsenious acid, which accompanies the sulphurous acid into the lead-chambers, and there contaminates the sulphuric acid. If such acid is used in the production of soda, the arsenic passes partly into the hydrochloric acid and the soda.

Composition of the Roasting Gases.—480 kilos. of iron sulphide require $(11 \times 32) = 352$ kilos. or $(11 \times 22{\cdot}3) = 245{\cdot}3$ cubic metres oxygen, and give $(8 \times 64) = 512$ kilos. or $(8 \times 22{\cdot}3) = 178{\cdot}4$ cubic metres of sulphurous acid. We, therefore, do not obtain—as on burning sulphur—the same volume of sulphurous acid, but from 100 litres oxygen only 72·7 litres sulphurous acid. With blende:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2,$$

100 litres oxygen yield only 66·7 litres of sulphurous acid.

Fig. 255.



On burning sulphur in atmospheric air, the mixture of gas obtained may theoretically contain 21 volumes per cent. of sulphurous acid, whilst the roasting gases from pyrites can contain at most 15·2 and from blende 14 per cent. sulphurous acid.

In point of fact, this percentage is not reached, since a part of the sulphurous acid forms always SO_3 (or, owing to atmospheric moisture, H_2SO_4). In burning sulphur this production of sulphuric acid is generally trifling, but with pyrites it may amount to 20 per cent. of the existing sulphurous acid. If the sulphurous acid is to be used as such, this circumstance involves a considerable loss.

Liquid Sulphurous Acid.—For the production of liquid sulphurous acid the process of Hänisch and Schröder holds good. The roasting gases, &c., pass through the pipe *a* (Fig. 255), into the scrubber, *b*, charged with pieces of coke, over which a rain of cold water trickles down and dissolves the sulphurous acid. The non-dissolved gases, N and O, escape at *c*. The watery solution of sulphurous acid flows continuously through the pipe *d* into a series of closed lead pans, *e*, in which it is heated to a boil. The escaping vapours of sulphurous acid arise through the tube *f*, at the cooling worm, *g*, which is surrounded by cold water, and from here through the pipe *h* into the pan *i*, into which sulphuric acid is injected to free the sulphurous acid perfectly from moisture. From the pan *i*, the gases pass through the tube *k* to the pump, *l*. The liquid in the lead

pans, *e*, which still holds small quantities of sulphurous acid in solution, passes for further treatment, through the pipe *m*, into the recipient, *n*, in which are placed nets of lead wire, and flows in the form of rain to meet a current of steam, which is introduced by the tube *o*. The fumes of sulphurous acid thus set free are carried off by the pipe *p*, opening into *f*, traverse the refrigerating worm *g* and the pan *i*, and unite with the remaining vapours of sulphurous acid in the pump, *l*. The water liquefied in the worm, *g*, flows back through *p* into the recipient, *n*, and is let off as required through the pipe *q*. In order to regulate the pressure in the installation, the taffeta bag, *r*, is introduced into the pipe *k*, the movement of the pump being regulated by the size of the bag. The gases compressed in the pump, *l*, pass through the pipe *s* into the refrigerating worm *t*, and are there liquefied. From the worm *t* the acid flows into the pan *u*, from which it is run off into strong bottles, *v*, fit for transport. In order to carry off the accompanying gases (O and N), there is connected with the pan *u* a pipe, *w*, provided with a valve, by which these gases are let into the scrubber, *b*.

This process is in operation, *e.g.*, at the zinc-works of Hamborn near Oberhausen. The sulphurous acid is despatched hence in pan-cans holding 100 hectokilos., or in so-called bombs, containing 5 hectokilos., and is used in manufactories of ice, in sugar-works, and in paper-mills for the production of so-called sulphite stuff.

The process is worthy of notice, with reference to the utilisation of the sulphurous acid which escapes in melting glass from sulphate:

$$Na_2SO_4 + C + SiO_2 = Na_2SiO_3 + CO + SO_2;$$

in the manufacture of ultramarine, &c.

Much inferior are the processes of Pictet, who boils sulphur with sulphuric acid, and of Hart, who boils iron pyrites with sulphuric acid.

Properties.—Sulphurous acid is a colourless gas of a pungent odour which can be liquefied by pressure or by strong refrigeration. One litre water at 0° dissolves 79·8 litres (= 229 grammes), at + 10° 56·6, and at 20° 39·4 litres sulphurous acid. One cubic metre of sulphurous acid at 0° and 760 millimetres pressure weighs 2·86 kilos.

Sulphurous acid is a powerful blood poison. Air containing 0·04 per cent. by volume of SO_2 occasions difficulty of breathing.

In the presence of water all the higher oxides of nitrogen give off oxygen to sulphurous acid and convert it into sulphuric acid, being at the same time reduced to nitric oxide. Chlorine converts moist sulphurous acid into sulphuric acid. If mixed with sulphuretted hydrogen in presence of water, sulphurous acid deposits sulphur. In contact with zinc there is no escape of hydrogen, but sulphurous acid is converted to hydrosulphurous acid or hyposulphurous acid (H_2SO_2)—not to be confounded with the acid formerly called hyposulphurous acid, but now known as the thiosulphuric.

Applications.—Sulphurous acid is used in the production of sulphuric acid, of paper, of the madder preparations of E. Kopp (now almost obsolete); for preparing sodium thiosulphate, and for obtaining sulphate from sodium chloride; for opening up alum shales in the manufacture of alum; for extracting copper from certain ores; for dissolving auriferous and argentiferous iron ores; for extracting calcium phosphate from bones and minerals; for preserving fruits, beer, wines, hops, meat, syrups of dextrine, saccharine juices, &c.; as a disinfectant; for preparing ice; for bleaching silk, wool, sponge, feathers, glue, gut strings, isinglass (which are turned yellow by chlorine), baskets, straw-tissues, gum arabic, &c. The bleaching action of sulphurous acid may be reduced to two different causes; in most cases the colour is merely masked, but in others it is destroyed. The colouring-matters of most red and blue flowers, fruits, &c., form with sulphurous acid colourless combinations, but the colour still exists. A rose bleached by sulphurous acid recovers its original red tone if moistened with dilute sulphuric acid. The colouring matters of yellow flowers are indifferent to sulphurous acid, and are not bleached. Many colours, such as indigo blue, carmine, and the

natural yellow of silk, are not at first bleached by sulphurous acid, but a subsequent bleaching is effected when the oxygen present is ozonised under the influence of light, and effects a destruction of the colours. The deoxidising power of sulphurous acid has been used of late for extinguishing fires.

Sulphurous acid, as furnace smoke—and indeed coal-smoke—has a destructive action on vegetation. Its continuous escape blights the fields and destroys entire forests; coniferous trees are especially sensitive to sulphurous acid.*

Calcium Sulphite, $CaSO_3$, and calcium bisulphite are obtained by passing the sulphurous acid obtained by burning sulphur or roasting pyrites into towers filled with limestone whilst water trickles down from above, or, better still, by passing sulphurous acid into milk of lime. The acid solution is extensively used for the production of "sulphite stuff," *i.e.*, vegetable fibre treated with a bisulphite, for the paper manufacturer.

The uses of sodium bisulphite (leukogene) are much the same as those of the free gaseous sulphurous acid. It bleaches fine woollen and worsted goods in a better manner.

Sodium Thiosulphate.—This compound, $Na_2S_2O_3,5H_2O$ (formerly known as sodium hyposulphite), may be prepared in several ways. Kopp first produced calcium thiosulphate by passing sulphurous acid over the vat-waste of alkali works, and decomposed the lime salt thus obtained by a solution of sodium sulphate, when gypsum is precipitated and sodium thiosulphate remains in solution.

It has the important property of forming, with silver oxide, a readily soluble double salt (silver sodium thiosulphate, $NaAgS_2O_3$), thus readily dissolving insoluble silver compounds, such as silver iodide and chloride, whence its application in photography and in the metallurgy of silver. Sodium thiosulphate dissolves iodine in large quantity, whence its application in chlorometry and generally in the iodometric methods. A solution of sodium sulphite mixed with thiosulphate dissolves malachite and azurite in the state of cuprous sodium thiosulphate—a property utilised by Stromeyer for the extraction of copper. In sulphuric acid works it is sometimes used to remove arsenic from the chamber acid, being transformed along with arsenious acid into arsenic sulphide and sodium sulphate. It is also used for preparing mercurial and antimonial vermilion, for obtaining aldehyde-green (emeraldine), for dyeing wool with eosine, as well as (Lauth, 1875) for a mordant in dyeing wool a methyl-green. Lead and also copper thiosulphates are successfully used for non-phosphoric matches.

The determination of free sulphurous acid in presence of sulphides is effected according to the equations:—

$$1.\ SO_2 + 2H_2O + 2I = H_2SO_4 + 2IH.$$

$$2.\ Na_2SO_3 + H_2O + 2I = Na_2SO_4 + 2IH.$$

$$3.\ CaSO_3 + SO_2 + 3H_2O + 4I = CaSO_4 + H_2SO_4 + 4IH.$$

There is formed hydriodic acid in quantity equivalent to the iodine used; the sulphurous acid becomes sulphuric acid. If the sulphurous acid was free there is produced a corresponding quantity of free sulphuric acid. If at the end of the titration with iodine the total quantity of the free acids is determined alkalimetrically and that of the hydriodic acid is deducted, we obtain the quantity of the free sulphuric acid formed, and, consequently, that of the free sulphurous acid. This process is suitable for the determination of the sulphuric acid of the pyrites furnace gases, if the decolorised solution of iodine resulting from the determination of the sulphurous acid of the gases is titrated with decinormal soda. What more is used than corresponds to the acids formed from SO_2 and iodine, shows the sulphuric acid present in the furnace gases.

* The only remedy is to utilise the heat of fuel better, thus reducing the quantity of coal consumed. "Smoke consumption" is not of the slightest use in this respect. In manufacturing processes, the sulphurous acid given off may in many cases be absorbed by passing it through lime.

SULPHURIC ACID.

Three kinds of sulphuric acid are distinguished in manufactures and in commerce:

a. The fuming or Nordhausen sulphuric acid, distilled (formerly) from ferric sulphate, or obtained by dissolving sulphuric anhydride in ordinary sulphuric acid.

b. Solid oil of vitriol and sulphuric anhydride.

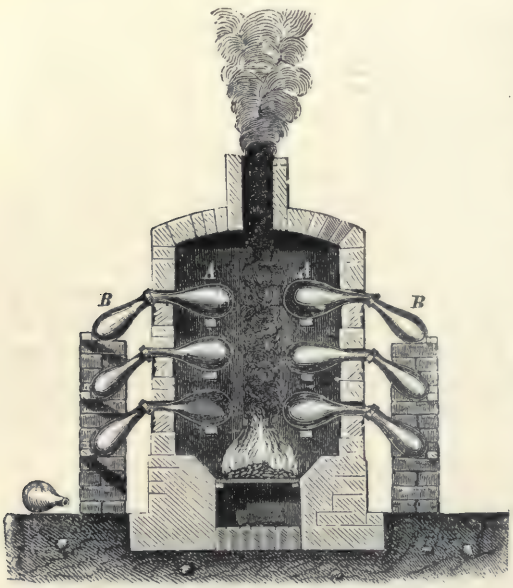
c. Ordinary sulphuric acid.*

Fuming Sulphuric Acid.—At a red heat all the sulphates, except those of the alkalies and alkaline earths, are decomposed, giving off vapours of sulphuric acid (or of sulphurous acid and oxygen). Ferrous sulphate was formerly preferred on account of its cheapness. At a red heat it is decomposed into ferric oxide, sulphuric anhydride, and sulphurous acid: $2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$.

Sulphuric anhydride could be obtained in this manner, if it were possible to keep it free from water, on the large scale. Water, however, always remains behind, and there is consequently obtained the so-called fuming acid, a variable mixture of sulphuric anhydride (teroxide, SO_3) with sulphuric acid (H_2SO_4), or a mixture of sulphuric acid with pyrosulphuric acid ($H_2S_2O_7$) in varying proportions. In the Bohemian vitriol works there is used the very impure copperas (ferrous sulphate) obtained by boiling down the mother liquors, which contain a considerable quantity of ferric sulphate. The decomposition of the anhydrous salt proceeds as follows:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

Fig. 256.



The preparation of fuming sulphuric acid from sulphur shales (vitriolic slate) is effected in Bohemia as follows:—The shales are allowed to weather by prolonged exposure to the air and are then lixiviated. The pyrites present in the shales is oxidised first to ferrous sulphate, and then to ferric sulphate. The lye obtained is evaporated to dryness and dehydrated, as far as possible, in pans. The dry, fused saline mass (vitriol stone) is a hard, greenish-yellow mass, which is further heated in a reverberatory in order to convert the remaining ferrous sulphate to ferric sulphate, and is then ignited in the burning stoves (Fig. 256). This is a galley furnace, in which there are two ranks of fire-clay flasks, the necks of which are built in such a manner that the mouths of the receivers can be applied and luted on. When the flasks, each of which contains 1¼ kilo. of the mass, have been charged, heat is applied. The watery sulphuric acid, containing sulphurous acid, is not generally collected. But as soon as white vapours of anhydrous sulphuric acid appear, the receivers are fixed and luted on and the distillation begins. The process takes from twenty-four to thirty-six hours. The flasks are then

* This last kind, known on the Continent as English sulphuric acid, is technically spoken of in this country, when undiluted, as oil of vitriol, or double oil of vitriol, D.O.V.

charged afresh, and the same receivers are applied with the acid which has already passed over. After four repetitions the acid has the proper concentration. The residue is red ferric oxide (colcothar, Paris red). The yield of fuming acid is about 45 to 50 per cent. of the weight of the dehydrated vitriol stone. Instead of distilling the vitriol stone, a ferrous sulphate is sometimes used, prepared from colcothar or burnt ore, and sulphuric acid, the iron oxide remaining in the flasks being used again.

The sodium bisulphate ($NaHSO_4$) remaining as a residue on preparing nitric acid from soda-saltpetre is also used for the manufacture of fuming sulphuric acid. When heated to fusion, this compound gives off water and sodium; pyrosulphate remains, and on further heating to about 600° the latter is split up into sulphuric anhydride and neutral sulphate: $Na_2S_2O_7 = SO_3 + Na_2SO_4$. The anhydride is passed into sulphuric acid. Wolters recommends for the preparation of the anhydride a mixture of magnesium sulphate and sodium pyrosulphate. Far below a red heat, sulphur teroxide is set free, and there remains a double salt, $MgSO_4 + Na_2SO_4$, which is separated into its constituents in the known manner, and returns to the circuit of the manufacture.

Properties.—Fuming sulphuric acid is a light-brown, thick, oily liquid, of spec. gr. 1·86 to 1·89, and consists of a solution of the anhydride in sulphuric acid, from which the anhydride evaporates even at common temperatures, forming white clouds in moist air. In the cold, pyrosulphuric acid separates from it as a crystalline mass, fusible at 35°, which, if gently heated, is resolved into sulphuric anhydride and sulphuric acid:

$$H_2S_2O_7 = SO_3 + H_2SO_4.$$

Formerly it was used only for dissolving indigo (1 part indigo is soluble in 4 parts of the fuming acid). Recently it has been used to a larger extent in the treatment of ozokerite and in the production of various tar-colours, *e.g.*, for preparing benzol disulphonic acid, by heating benzol with fuming sulphuric acid in the manufacture of eosine.

Solid Oil of Vitriol.—For some years pyrosulphuric acid, $H_2S_2O_7$, has been met with in commerce. It is obtained by dissolving 1 mol. anhydride in 1 mol. sulphuric acid, $SO_3 + H_2SO_4 = H_2S_2O_7$.

Sulphuric anhydride is obtained either by heating ferric sulphate, perfectly dehydrated, or Wolter's mixture, or by warming strong fuming sulphuric acid; or, according to Winkler, synthetically ($SO_2 + O = SO_3$), by resolving sulphuric acid at a red heat into sulphurous acid, oxygen, and water, the latter being kept back by means of concentrated sulphuric acid, the mixture of sulphurous acid and oxygen being passed over ignited platinised asbestos, where it is again converted into sulphur teroxide. Messel and Squire, of London, use platinised pumice. The real anhydride, SO_3, is at common temperatures a colourless liquid, which below + 16° solidifies to felted asbestos-like needles, and boils at 46° to 47°. The so-called anhydride of commerce, which is sold in sheet-iron boxes containing 60 kilos., consists of 98 per cent. anhydride and 2 per cent. H_2SO_4.

Ordinary Sulphuric Acid.—By far the largest quantity of sulphuric acid is prepared by the oxidation of sulphurous acid obtained on the combustion of sulphur, or on roasting pyrites and blende; the oxidation is effected by means of nitric acid. According to the equation, $S_2 + 3O_2 + 2H_2O = 2H_2SO_4$, 64 kilos. of sulphur require 67 cubic metres of oxygen, or 320 cubic metres of atmospheric air, along with 36 kilos. of watery vapour, in order to yield 196 kilos. sulphuric acid. For the production of sulphuric acid the roasting gases must contain to 100 vols. sulphurous acid at least 50 vols. oxygen. In fact, an excess of oxygen must be present if the reactions are not to be too slow. With regard to the sulphuric acid already formed, the gases from sulphur when passed into the lead-chambers contain 12 per cent. by volume of sulphurous acid; if from pyrites, 7 per cent.; if from blende, 6 to 7 per cent.

Lead-Chambers.—As long as we are compelled, in the manufacture of sulphuric

acid, to use the requisite substances as gases, and especially to use oxygen in the state of atmospheric air, large chambers are necessary, which must be cheap to construct, air-tight, and must consist of a material not attacked by the nitrous gases and vapours or by sulphuric acid.

Among the many materials which have been proposed, one only, lead, fulfils most of these demands. In the Fouché-Lepellitier works at Javel, near Paris, a gutta-percha chamber was in use in the years 1860–1870.

As to the sort of lead which is most suitable for the construction of chambers, it is generally assumed that metals are the less easily attacked by an acid the purer they are. Careful researches, however, proved that lead is attacked by sulphuric acid the more readily the purer it is. On the other hand, according to a communication from J. Glover, in order to test the suitableness of lead for the construction of chambers, sheets of different alloys were placed for 110 days in a lead-chamber. Pure lead was found to lose 7·5 per cent. Lead alloyed with copper and antimony experienced the following losses:—

Copper.	Loss.		Antimony.	Loss.
0·1 per cent.	7·1 per cent.	...	0·1 per cent.	8·1 per cent.
0·2 „	7·1 „	...	0·2 „	9·2 „
0·3 „	7·5 „	...	0·3 „	10·9 „
0·4 „	9·1 „	...	0·4 „	11·6 „
0·5 „	8·5 „	...	0·5 „	11·9 „

N. Cookson heated lead with sulphuric acid of different strengths. He found that strong acids at high temperatures attacked antimoniferous lead more than pure lead, but weaker acid at lower temperatures attacked antimoniferous lead less than pure lead.

It has been repeatedly observed that some coleopterous insects perforate the plates of the chambers. At the Mulden works, wood wasps have made holes in the lead.

The lead is rolled out in plates 0·6 metre in breadth, and of a thickness of 3 to 8 millimetres. The chamber consists of two parts: the bottom, which has a plate-like form, and is bent up on all sides to the height of 36 to 54 centimetres; and the side walls, consisting of one piece, which stand upon the bottom like a bell. Both these parts are made of a great number of sheets soldered together. The chambers are secured in a frame of woodwork, consisting of uprights, horizontal beams, &c. The sides are first covered with lead sheets, which are soldered together at the edges by the autogenous process. After the sides are completed, the bottom and the top are covered with lead plates. On the outside of the chamber several strips of lead, from 18 to 20 centimetres in breadth and 36 centimetres in length, are soldered fast and secured to the woodwork with iron nails. The covering plate is secured, in the same manner, to beams which run across the chamber.

The bottom of the chamber is always covered with acid; the lower corners of the side walls dip freely into the liquid, forming a hydraulic joint. Hence, acid can be drawn off at any time, and in any place. In and on the chambers there are arranged man-holes in the sides (for executing repairs), pipes for conveying the gases from the furnaces and steam from the boiler, pipes for carrying off the chamber gases, glass discs for observing the state of the chambers and the progress of the formation of the acid, generally placed in two opposite walls in the direction of the incident light; hydrometers and thermometers, the latter of which are attached to the sides for the estimation of the temperature at different parts of the chamber. In order to take, from time to time, specimens of the acid which is being formed, there are in some works so-called dropping-tables, which, at the height of 1 metre from the bottom, support a bent plate with a turned-up edge, 0·6 metre in length and 0·5 metre in breadth. The acid which collects upon this plate is conveyed through a lead tube to a

beaker placed outside the chamber, for the determination of its strength. The chambers are covered in with a roof, which is necessary in Germany, Belgium, and France, whilst in Britain, as the temperature varies much less at different seasons of the year, the chambers commonly stand in the open air. In recent works the chambers are often supported on pillars of masonry, so that the space below is available for the erection of pyrites kilns, &c.

Arrangements for collecting the Nitrous Vapours.—In order to reduce the loss of nitre as far as possible, the nitrous constituents (nitrous and hyponitric acid) are withdrawn from the gases and vapours escaping from the chambers before they can pass out into the air, and are thus made again available for the process of acid forming. This object is effected almost everywhere by means of sulphuric acid in the absorbent coke-tower proposed by Gay-Lussac. This consists of a cylinder of lead about 10 metres high, closed gas-tight above, and standing below, like the chambers, in a lead vessel, filled with acid, so as to form a hydraulic joint (Fig. 257). The inner walls of such

Fig. 257.

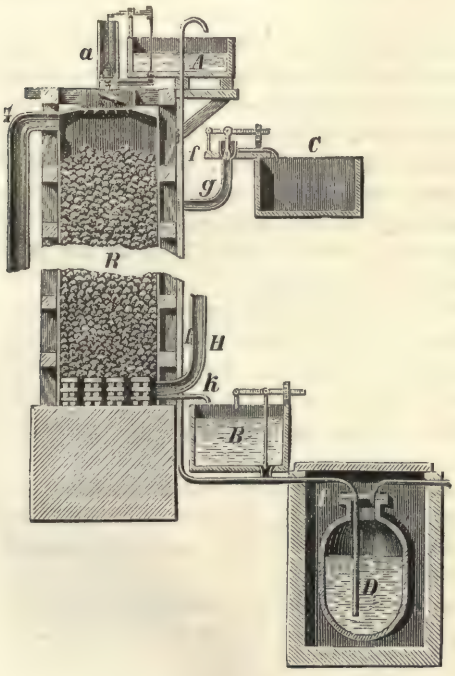
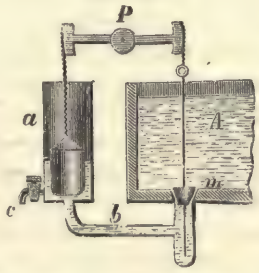


Fig. 258.



cylinders are often lined with thin fire-proof stones. The tower is filled with coarse pieces of coke, but sometimes glass balls, pieces of broken drain-pipes, &c., are used. The distribution of the sulphuric acid over the pieces of coke is effected by means of the cistern *A*, from which a stream of acid flows uninterruptedly into an oscillating trough fixed over a lead-plate with about twenty tubes. From these tubes the acid flows into the tower. For securing a constant outflow of acid the Mariotte bottle is often used, or the apparatus shown in Fig. 258. At the side of the acid cistern, *A*, is a small lead cylinder, *a*; the tube *b* is conical at its mouth and secured acid-tight by means of a leaden plug, *m*, of suitable shape. This plug is fixed on an iron rod, the part of which below the plug is to guide it in its upward and downward movements and to make it always fall exactly into the opening. In the lead cylinder there hangs a lead jug, fixed to a lever by means of a chain, which at its other end is connected by a short chain with the rod of the lead plug. When the apparatus is to act, the cistern *A* is filled with acid, and the plug is fixed in the aperture. If the sulphuric acid is to flow into the tower at a uniform pressure the lead jug is drawn up in the cylinder and its chain is secured to the beam, *P*, which is set horizontally. The plug-rod is now also secured to the beam. If the jug is left to itself the plug is raised, the sulphuric acid flows through the tube *b* into the lead cylinder, and the jug rises swimming on the acid in proportion as the level of the acid rises. As soon as the jug has been raised 18 to

20 centimetres the plug sinks and closes the tube *b*. If the cock, *c*, in the cylinder is opened the sulphuric acid sinks, and with it the jug; thereby the plug is lifted, and the level in the lead cylinder is restored by an inflow of sulphuric acid. If the outflow cock, *c*, is suitably placed, the sulphuric acid flows at a uniform pressure into the coke-tower, supposing that the level of the acid in the cistern *A* never falls below 18 centimetres.

The sulphuric acid is forced up from the monte-jus, *D*, through the pipe *b*, into the cistern *A*. The gases coming from the lead chambers stream into the coke-tower at *H*, and pass out again at *G*, after having lost their nitrous constituents. The sulphuric acid, charged with these ingredients (nitrose), runs from the dish of the absorption-tower through the pipe *k*, into the cistern *B*, and thence into a monte-jus, which convey it into the denitrifying apparatus.

In the works of Fikentscher, at Zwickau, the absorption apparatus consists of eight stoneware pipes, set above each other, of 0·8 metre in height and in width; each open above, and provided with a perforated bottom. On each pipe there are three inclined planes of stoneware, on which sulphuric acid of 130° Tw. trickles down as it enters in drops.

In order to test the remarkable phenomenon that this so-called nitrose of the Gay-Lussac tower contains only nitrous acid, even when the entering gases show considerable quantities of hyponitric acid, G. Lunge examined the action of coke upon nitric acid. Experiment showed that, in contact with coke, the nitric acid, dissolved in the sulphuric acid, was almost completely reduced to nitrous acid, slowly at common temperatures, but very rapidly at such a temperature as generally prevails in the Gay-Lussac tower. Whether this is immediately effected by the carbon or by its action upon sulphuric acid (with the production of sulphurous acid), or by the joint action of iron sulphide present in the coke, remains undecided.

The absorptive power of sulphuric acid for nitrous acid differs greatly according to its concentration. Acid of 154° Tw. is able to dissolve more than three times as much nitrous acid as that at 130° Tw. So that, in using the stronger acid, there is the advantage that only one-third of the usual quantity of acid is necessary. Besides, the greater affinity of concentrated acid for the nitrous vapours is a greater guarantee for their complete absorption.

Denitration of the Nitrose.—The acid flowing out of the absorption-tower, the nitrose, is a solution of nitrosulphonic acid, $SO_2.OH.NO_2$, in sulphuric acid. The problem is to decompose this nitrose into the nitrous compounds and into pure sulphuric acid, using the former again in the chamber process.

The earlier denitrating appliances all depended on diluting the nitrose with hot water or steam, or with both together. The nitrosulphonic acid of the nitrose is resolved into sulphurous acid and nitric acid.

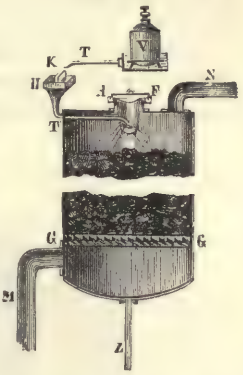
This decomposition can be effected in the stage-apparatus, in Gay-Lussac's denitrificator, in the boiling-drum, or in the cascade.

The stage-apparatus is a small lead chamber, of a few cubic metres capacity, in which five successive lead floors are soldered at different heights. They leave alternately, at opposite sides of the chamber, a passage free for the sulphuric gases, which enter beneath the lowest floor, traverse the apparatus in zig-zag, and above the highest stage pass into the lead-chamber through a pipe. The nitrose enters through the cover of the apparatus by a cock, falls upon the highest floor, then upon the second and third, coming in contact with the sulphurous acid all the way, and is denitrated at the foot of the apparatus, so that it may be either drawn off directly or conveyed into the first lead-chamber.

Gay-Lussac's denitrificator consists of a tower of sheet-lead, into which the furnace gases enter by the pipe, *M* (Fig. 259), and diffuse themselves under the grating, *G*,

upon which rests a bed of coke. The nitrose crosses from the cistern, *V*, and is distributed over the coke, trickling downwards to meet the ascending gases, and passing out denitrised at the bottom of the tower through the tube, *t*. Both in the stage apparatus and in this tower apparatus steam is introduced, which distinguishes both from the Glover tower.

Fig. 259.



The denitrising apparatus devised by J. Glover, of Wallsend, is now almost universally used under the name of the Glover tower.

In the first place, this tower serves as a concentrating and cooling apparatus, as hot sulphurous acid is conveyed into the tower whilst chamber acid meets the hot gases. Thus the sulphurous acid is cooled and the chamber acid concentrated. The watery vapours evolved pass into the lead chambers, effecting a considerable saving in steam for the working of the chamber. Besides, the Glover tower denitrises the nitrose which is decomposed by the joint action of the steam and the sulphurous acid, so that the concentrated sulphuric acid running off below is denitrised, and the nitric oxide, set free, enters the chamber again, where it again mediates the formation of sulphuric acid.

In the Glover tower the chief part of the sulphuric acid present in the roasting gases is separated out, so that by this arrangement the performance of the lead-chambers is decidedly augmented.

Recently the Glover tower has been also used for bringing the nitric acid required in the sulphuric acid process into contact without any special apparatus.

Fig. 260.



Fig. 262.

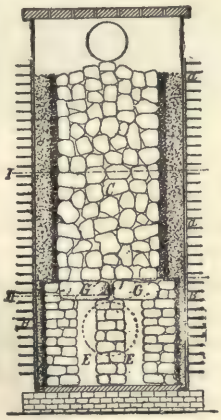


Fig. 261.

Explanation of Terms.
Schnitt I—Section I.
Schnitt II—Section II.

The Glover tower is built of strong lead plates, surrounded with a frame of wood. To protect the lead walls there is a lining of fire-tiles which is stronger in the lower part of the tower than in the upper half. The tower is filled with bricks set like a grating, or with fragments of quartz. At the top of the tower are two cisterns of wood lined with lead, the one containing nitrose and the other the chamber acid to be concentrated. For the even distribution of each acid there is a small Segner's wheel provided, made of glass, which is caused to rotate by the outflow of the acid which it distributes. It is arranged that both acids meet within the tower and flow out together. The roasting-gases traverse the tower from below upwards and then enter the lead-chamber.

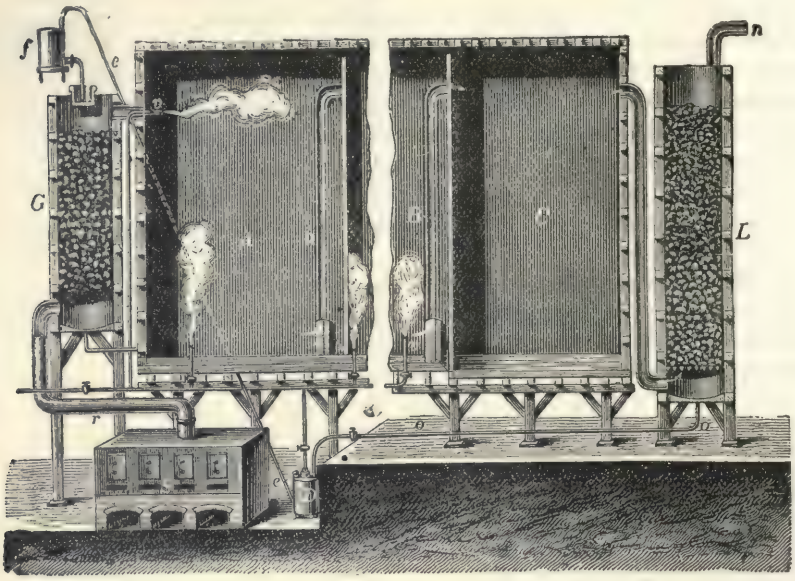
According to Herreshof, there are erected in the tower (here drawn as greatly shortened) cross walls, *E* (Figs. 260, 261, 262), over which large pieces of quartz, *G*, are laid across and form a vault. Upon these are laid quartz stones, *C*, to a certain depth so that they leave a space of 300–400 millim., next to the lead wall of the tower, *B*, All large gaps on the side of the heaped-up material are filled with smaller pieces of quartz, and around them is laid a thin layer of quartz-sand, which during the building is kept in its place by means of iron plates. The remaining space between the filling

and the lead wall is filled with rather fine quartz-sand, which completely prevents the acid from touching the lead. Iron plates, *a*, are secured on the corner pillars, *b*, so that the lead casing may bear the weight.

The Glover tower is the simplest and cheapest apparatus for concentrating and denitrification, as in it sulphuric acid can be brought to a strength of 137° or even 145° Tw.

The general arrangement of a sulphuric acid works is shown (diagrammatically) in Fig. 263. The sulphurous acid evolved in the furnace, *S*, from sulphur, pyrites, or blende is let pass through the pipe, *r*, into the bottom of the denitrising apparatus, *G*, over

Fig. 263.



the contents of which the nitrose and—in case nitric acid is not evolved in the furnaces, *S*, from nitre and sulphuric acid—the requisite quantity of nitrie acid trickles down. The concentrated acid flows off below, and is conveyed away if it is not forced up by the monte-jus to the cistern of the Gay-Lussac tower, *L*.

The gases pass now, along with the steam entering by the tube *v*, into the first lead-chamber, *A*. What is not condensed here passes from the bottom through the tube *b*, into the upper part of the second lead-chamber, *B*, and then in like manner into the third, *C*, escaping from here into the Gay-Lussac tower, *L*, and finally go off at *n*. The three chambers may be built either separate or together, as the figure shows. The sulphuric acid formed (chamber acid) is led off for further treatment. The nitrose formed in the closed Gay-Lussac tower, *L*, flows through *o* into the monte-jus, *D*, and thence by means of compressed air (less suitably by means of steam) it is forced through the pipe *e* into the cistern, *f*, whence it arrives into the Glover tower, *G*.

We must notice Laurent's apparatus for raising sulphuric acid. It consists of a tube of lead, vulcanite, or glass, which branches off directly from the recipient to be emptied, descends more or less deeply, according to the height to which the liquid is to be lifted, and then ascends to the cistern to be fed above. The compressed air is introduced at the bottom of the longest part by a very small pipe which ascends high enough to prevent the entrance of the liquid into the apparatus for compressing the air. This arrangement is especially convenient for raising up the acid to the Glover towers.

Mactear recommends the form shown in Fig. 264. So much air is forced in through

the pipe, *a*, that the mixture of acid with air in the ascending pipe, *S*, is raised by the column of the affluent acid. The air escapes at *v*, and the acid flows off at *e*. If no compressed air is accessible, a Körting suction blast is attached to the tube *v*, and sucks up the necessary quantity of air through the tube *a*. If the acid is to be lifted higher, a monte-jus is used and a part of the compressed air is allowed to enter into the tube *S*, in order to drive the acid two or three times the height corresponding to the pressure of the compressed air.

If the liquid has to be taken from a flat cistern, *n* (Fig. 265), it is let flow into a wide tube, *c*, closed below, whilst air is driven in through a narrow tube, *a*; the mixture of acid and air rises up in the tube *e*, which is open below.

The working of a newly installed sulphuric acid plant begins by pouring upon the bottom of the chambers sulphuric acid of spec. gr. 1·45 (90° Tw.) to such a depth that the walls of the chamber may dip into the acid for about 3 centimetres. If the bottom has been soldered to the sides, the depth of the acid must be 12 to 18 centimetres.

Fig. 264.

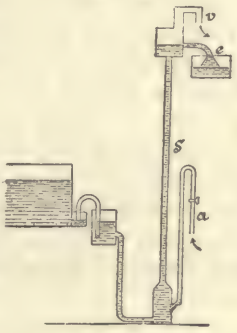
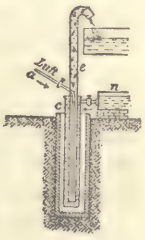


Fig. 265.



After the floor of the chamber is thus covered with acid, the air is expelled from the system of chambers by admitting sulphurous acid from the pyrites furnaces, which will by this time have come into action. Then, according to the kind of working, either liquid nitric acid is allowed to enter or nitric acid vapour is developed from the nitre pots in the sulphur furnaces. At the outset nitre is used in excess (10 to 15 per cent. of the weight of the sulphur), afterwards in the normal proportion of 4 to 6 per cent. as soon as the temperature of the walls is observed to rise, which is generally in about twenty-four hours. When the formation of sulphuric acid has set in, which may be known by the dew of condensed acid on the walls (within) of the lead-chamber and the plugs of the trial-holes, the time has arrived for the admission of steam.

The chambers are now observed three to four times daily, noting the height of the thermometers and testing the acid formed and the gases passing in and out.

In general, the proportion of SO_2 in the gases which enter is determined by means of iodine solution, according to Reich. In the summer of 1876 the author repeatedly examined the gases evolved on roasting smalls in a plate furnace. In order to determine the proportion of sulphuric acid vapour and of sulphurous acid, he used in his apparatus for examining smoke gases, petroleum instead of water, the sample of gas being drawn up through a porcelain tube as quickly as possible after measurement into the potassa tube, and after dissolving the acids into pyrogallate to determine the oxygen. In another portion drawn simultaneously SO_2 was determined by the process of Reich.

A series of experiments, conducted at the works of Meyer and Riemann, near Hanover, July 19, 1876, gave:

Place of Sample.	SO_2 by I.	Total Acids.	O.
Plate 2 from below	0·96	1·4	18·4
„ 4 „	1·52	2·2	16·6
„ 6 „	3·81	4·6	12·5
Collecting pipe	7·53	8·6	7·5

The gases escaping from the Gay-Lussac contained 0·4 per cent. acid gases and 4·4 per cent. oxygen.

This volumetric process makes no pretensions to great accuracy; indeed, the real

proportion of sulphuric acid will be rather greater. It has, however, the advantage that it shows in four or five minutes the total quantity of acids approximately, and the oxygen accurately, to about 0·2 per cent. The apparatus for the determination of SO_2 seems more suitable for checking the work than the method of Reich, as the proportion of sulphuric acid often exceeds 2 per cent. by volume. The determination of oxygen in the exit gases deserves attention, as irregularities may thus be quickly and accurately detected. The supply of air to the pyrites furnaces must be so regulated that the gases issuing from the Gay-Lussac contain 3 to 6 per cent. oxygen.

In the lead-chamber in which the production of sulphuric acid is chiefly effected, a thermometer, hanging at about 1½ metre from the ground, should indicate a temperature of 40° to 50°. If the chambers grow too hot, less nitre (or nitric acid) is taken; if they are too cold, more must be added. If an excess of steam is used, there is formed a dilute acid, which takes up nitric and nitrous acids and corrodes the lead; sulphurous acid also may be taken up. If there is a deficiency of steam, nitrous acid is formed, and leads to the formation of so-called chamber crystals. The strength of the acid formed in the lead-chamber shows whether the influx of steam is normal or abnormal. If the acid taken in the first third of the chamber has a sp. gr. of 1·60 = 120° to 121° Tw., the right quantity of steam is being admitted.

The mud (so-called white lead) collecting in the chambers, which must be removed from time to time, varies greatly in composition, and is formed by the action of the acids upon the lead and its impurities, as well as matter introduced from the furnaces in the shape of flue-dust. It often contains selenium, sometimes thallium and indium.

Lead-Chamber Process.—According to F. Hurter, the following main equations regulate the process:—

$$SO_2 + H_2O + O + NO_2 = H_2SO_4 + NO_2 \text{ and,}$$
$$SO_2 + H_2O + O + N_2O_3 = H_2SO_4 + N_2O_3.$$

He shows that the work done in a system of chambers depends essentially on the quantity of nitrogen compounds contained in the gases and on the strength of the acid produced. The work of the succeeding chambers diminishes almost in a geometrical series. The same must be said of the excess of temperature of the chambers over that of their surroundings. The temperature of the first chamber of a system depends on what fraction of the entire system is taken up by its space.

According to the experiments of Lunge and Naef, in a normal state of the chambers the proportion of sulphurous acid diminishes very rapidly from the entrance to the middle of the first chamber, *i.e.*, from 7 to 1·7 or 1·9 per cent.; hence here 70 per cent. of the sulphurous acid has already been converted into sulphuric acid; this agrees well with the results of earlier observers, and with Hurter's theory. From the middle to the end of the first chamber, the SO_2 decreases very little, corresponding to a conversion of about 4 per cent. of its initial quantity into sulphuric acid. With the entrance into the second chamber, the reaction is suddenly intensified, and at its middle there is only from 0·2 to 0·4 per cent. sulphurous acid present, so that in this way 20 per cent. has been converted into sulphuric acid. From here to the end of the system, on account of the great dilution of the gases, and to reach a practical maximum (it is never absolutely complete), considerable chamber space is still needed. If the supply of nitre-gases is insufficient, the proportion of sulphurous acid decreases less rapidly, and the process goes on more in the second and third chamber.

Hence it appears that the formation of sulphuric acid goes on in the outset with great energy, that it grows very sluggish at the back of the chamber, and that in the second chamber the reaction is intensified. The only explanation to be found is that in the last part of the first chamber, owing to the dilution of the gases with 90 per cent. nitrogen, the molecules of sulphurous acid do not find sufficient N_2O_3 and O, which are again accumulated in other parts, but that, on passing through the pipe

leading into the second chamber, an intimate mixture of the gases is effected, so that the molecules of the three active gases are again brought sufficiently close to react upon each other. Hence the best system should be a larger number of smaller chambers. Certainly, doubtless with a regard to the economy of lead and of room, this system has of late been abandoned, and in some works the entire system has been made to consist of a single large chamber. But such attempts cannot have proved successful, as they are very uncommon, and some who had adopted the one-chamber system have gone back to the use of several chambers. It seems that a frequent passage through connection-pipes, and the intermixture of gases thus effected, are advantageous. In the atmosphere of the last chamber, only N_2O_3 was found in normal working.

Formation of Sulphuric Acid in the Lead-Chambers.—According to G. Lunge, this process depends chiefly on the intermediate formation of nitrosylsulphuric acid. This is formed from sulphur dioxide, oxygen, and nitrous acid:

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2(SO_2,OH,ONO),$$

and is immediately, in contact with an excess of water, resolved into sulphuric acid and nitrogen trioxide:

$$2(SO_2,OH,ONO) + H_2O = 2SO_2(OH)_2 + N_2O_3,$$

which with water forms nitrous acid and water, so that the process is repeated. For the front part of the system of chambers we must also consider that here a part of the nitrosylsulphuric acid is denitrised by sulphurous acid:

$$2(SO_2,OH,ONO) + SO_2 = 2H_2O = 3SO_4H_2 + 2NO,$$

and that the nitrogen oxide formed in this manner with oxygen, sulphurous acid, and water forms directly nitrosylsulphuric acid:

$$2SO_2 + 2NO + 3O + H_2O = 2(SO_2,OH,ONO).$$

As a secondary reaction the latter can also be formed by the action of nitric acid (whether originally introduced or formed afresh) upon sulphur dioxide:

$$SO_2 + NO_2,OH = SO_2,OH,ONO.$$

The direct formation of sulphuric acid from sulphurous acid by the reduction of NO_2 and N_2O_3: $SO_2 + NO_2 + H_2O = SO_4H_2 + NO$; $SO_2 + N_2O_3 + H_2O = SO_4H_2 + 2NO$, certainly takes place to a trifling extent, though latterly this process is taken for the main reaction. Hyponitric acid does not occur in the normal chamber process, and nitric oxide appears only at the beginning, in virtue of a secondary reaction entering then in the direct reaction, of condensation: $SO_2 + NO_2.OH = SO_2,OH,ONO$.

Lunge does not view the chamber-process as an alternating reduction and oxidation of the nitrogen oxides, but as a condensation of nitrous acid or nitric oxide with sulphurous acid and oxygen to nitrosulphuric acid, and a splitting off again of the nitrous acid from the latter by the action of water.

Under certain circumstances nitrous oxide is known to be formed as a product of the reaction of sulphurous acid and nitrous acid. To this result the "chemical" loss of nitre in the manufacture of sulphuric acid—in contradistinction to the mechanical losses by imperfect absorption in the Gay-Lussac tower—and the nitrogen in the chamber acid are generally ascribed.

It cannot be theoretically denied that under very unfavourable circumstances the reduction of nitric oxide may go as far as to free nitrogen, but it has not been demonstrated in practice. It has been shown, firstly by R. Weber, then by Lunge, that the reduction of nitric oxide by sulphurous acid to N_2O occurs only in presence of water, or of sulphuric acid more dilute than that found in the chambers. Hence a formation of N_2O can occur only if an excess of water is present, which is very rarely the case, and with good work the "chemical" loss of nitre is very small, probably not 0·5 per cent.

Another abnormal reaction leads in practice to far more losses of nitre, namely, the formation of hyponitric acid in the last part of the system of chambers. This

causes the appearance of nitric acid in the bottom acid of the last chambers, but not, or very rarely, the nitrose of the Gay-Lussac tower, as it is here reduced by coke, perhaps with the co-operation of the last traces of sulphurous acid. It is said to have been observed in practice that under such circumstances red vapours escape unabsorbed from the Gay-Lussac tower. Lunge has shown that the formation of NO_2 is quite independent of the quantity of oxygen present, and that it occurs with abnormally low, with normal, and with abnormally high proportions of nitre. The process of the formation of sulphuric acid is then at an end before the gases have left the chambers. In the latter part of the system there is no mist of sulphuric acid, nor does there exist any appreciable quantity of sulphurous acid. The conditions for the normal process, as developed above, are, therefore, here wanting. The nitrous acid, which now meets with no bodies with which it can form permanent combinations, is by degrees dissociated in the large excess of air, and is partially oxidised to NO_2. The NO_2 comes in reaction with the bottom acid, and yields with it equal molecules of nitrosylsulphuric acid and nitric acid. Another portion of the NO_2 passes with the exit gases into the Gay-Lussac tower, and it was formerly said not to be here absorbed. This has been shown to be utterly erroneous, but it might easily happen that a coke-tower sufficient for ordinary circumstances is insufficient under such circumstances, and that, therefore, some nitric gas escaped into the air. It would be an abnormal condition of the chambers, with an excess of nitre-gases.

Much worse is the course of the chamber-process, if the nitre is insufficient, whether too little has been used at first, or that, in consequence of the inadequate size of the Gay-Lussac tower, the recovery of the nitrous acid is imperfectly effected. The formation of sulphuric acid is stopped at the back of the system, not, as in the last case, because the sulphurous acid is exhausted, but because there is too much. Now, therefore, a denitrification of the nitrosylsulphuric acid has to occur at this wrong place:

$$2(SO_2,OH,ONO) + SO_2 + 2H_2O = 3SO_4H_2 + 2NO,$$

and much nitric oxide is formed, the atmosphere of the chambers losing its yellow colour, either partly, or in very bad cases altogether. In all cases the temperature falls below the normal height, *i.e.*, that favourable for the formation of sulphuric acid, and, in spite of the presence of much oxygen, the combination of nitric oxide and sulphurous acid goes on very sluggishly. Water is often present in excess in the air of the chambers, and there is often nothing to prevent the nitric oxide from forming, with the oxygen and the water, nitric acid, which, as the temperature is here much lower, and there is much less sulphurous acid present than in the front part of the chambers, passes unreduced into the bottom acid, and makes the atmosphere of the chambers still poorer. Yet the bottom acid is not "nitrous" in the sense used by manufacturers, since it gives off no red fumes if mixed with hot water, because the nitrosylsulphuric acid is wanting. Also as sulphurous acid predominates, and there is almost no sulphuric acid in the air of the chambers, but only water, the formation of nitrous oxide (N_2O) goes on freely. This signifies a total loss of nitre; and equally lost is the nitric acid contained in the bottom acid if the acid is consumed directly, and the nitric oxide arriving unchanged in the Gay-Lussac tower is lost also. This still encounters oxygen, but not only is its quantity insufficient, but the excess of sulphurous acid acts here at the wrong place as a denitrifier, and can even destroy nitrosylsulphuric acid, if any is present. The nitric oxide escaping from the tower forms red fumes in contact with the air, whilst the "lantern" of the tower is white, as may often be observed. All these facts together lead, not only to great loss of sulphurous acid, and consequently to a poor yield of sulphuric acid, but also to a great loss of nitre, and involves a progressive impoverishment of the chambers in their stock of oxygen transferrers. Hence the well-known phenomenon which has been recently confirmed by Eschellmann, that if we have been too economical of nitre, and the above disease has attacked the chambers, it is necessary to add many times the

quantity of nitric acid which has been economised, in order to get them back into a normal condition.

It is important that these results take place at the *end* of the set of chambers. This is the reason why nitric oxide does not enter into the reaction, although, even when the chambers are working badly, there is almost always oxygen enough to convert the sulphurous acid into H_2SO_4. But in the first place the temperature is too low, probably far below the most favourable point, as the main reaction takes place at the hottest point of the system; secondly, there is no longer time for the molecules of oxygen distributed in a large volume of nitrogen to meet with the remaining substances in sufficient quantity; long before the oxygen is quite exhausted the gaseous mixture has arrived at the end of the system, and nitric oxide, sulphur dioxide, and oxygen escape together into the outer air, all diffused in a large excess of nitrogen.

Nothing in the practice of the sulphuric acid manufacture is more distinctly proved than that the process works satisfactorily only in presence of a large excess of oxygen and of nitrous acid, the latter of which is mainly recovered in the Gay-Lussac tower; if there is only a slight excess, sulphurous acid always escapes into the air. Even with a large excess of oxygen, a perfect oxidation of the sulphurous acid is impracticable. We seem to have reached the practically best limit when the exit gases contain only 0·5 per cent. of the sulphurous acid originally present. We have here to do with one of those reversible reactions whose progress can be turned in the desired direction by certain external conditions, such as the action of the mass of one of the ingredients, but can seldom be made absolutely complete. With an excess of oxygen and nitrous acid the reactions of condensation predominate—

$$2SO_2 + N_2O_3 + 2O + H_2O = 2SO_2.OH.ONO \text{ and}$$
$$2SO_2 + 2NO + 3O + H_2O = 2SO_2.OH.ONO;$$

therefore the conjunction of SO_2, N_2O_3, and O, characterised as the main reaction of the entire process, and H_2O to $SO_2.OH.ONO$; but if there is a relative excess of sulphurous acid the reactions of denitration predominate—

$$2SO_2.OH.ONO + SO_2 + 2H_2O = 3H_2SO_4 + 2NO,$$

by which the chamber crystals of sulphuric acid are again split up into H_2SO_4 and NO. The nitric oxide cannot further enter into reaction at the end of the system, and escapes unutilised, as the Gay-Lussac tower cannot retain it. This invertedre action corresponds to that which occurs with an excess of sulphuric acid: $SO_4H_2 + NOOH = SO_2.OH.ONO + H_2O$. If water is in excess we have the reaction: $SO_2 + OHONO + H_2O = SO_2(OH)_2 + NOOH$.

In the lead chamber process consequently a relatively large excess of oxygen and nitrous acid is necessary.

It is now intelligible how to a certain extent, according to practical experience, increased chamber room and an increased supply of nitre compensate each other. If under the other suppositions of the last described progress of a chamber, with an insufficient supply of nitre, the chamber room in one case is larger than in another, in the former case more molecules of sulphurous acid will meet with the necessary quantities of oxygen and the oxides of nitrogen than in the latter, because more time is given for intermixture; hence the excess of the two latter constituents need not be so large. As is well known in practice, the supply of oxygen must be carefully regulated by establishing the correct draught, and modifying it in accordance with any change of the atmospheric conditions.

In the sulphuric acid manufacture there is little left to be learned from theory. In the utilisation of the sulphur we have arrived nearly, or quite, at the utmost limit fixed by the inversion of the reaction, and the consumption of nitre can scarcely be brought below the small proportion with which the best arranged and best managed establishments are now working. We might perhaps desire to produce con

centrated acid at once in the chamber. But this attempt is opposed by theory as well as practice, and the wish is forestalled, since it is found possible by means of the Glover tower, or by utilising heat which would otherwise be lost, to obtain an acid containing 80 per cent. of monohydrate. In one direction only does progress seem possible. The chamber process, as now conducted, requires for the production of sulphuric acid a long time and, as a necessary consequence, extensive space.* It does not seem as if a diminution of time and space for the formation of sulphuric acid could be effected by any modifications of the temperature. The process might probably be abridged if a really effective system for the thorough and continuous intermixture of the gases were produced, so that the alternating play of the reactions might be effected at shorter intervals. Still more would this process be abridged if the dilution with nitrogen could be dispensed with by using pure oxygen in place of atmospheric air. Then a higher pressure would be practicable, which would render the reactions quicker and more intense. An easier condition would be to occasion a frequent collision of the gases with solid surfaces, whereby the particles which float as mist in the atmosphere of the chamber would soon condense to a fluid and settle to the bottom; a more rapid removal of the product and the reaction might favour the combination of the other ingredients, and might even promote the intermixture of the gases.†

Purification of Chamber Acid.—The sulphuric acid let off from the great chamber has an average sp. gr. of 1·52 = 104° Tw. or 50° B. This acid may be either used at once for opening up mineral phosphates in manure works, in the manufacture of ammonium sulphate, the manufacture of copperas, &c., or if it has to be carried away it can be evaporated down to the highest grade of concentration, 1·84 sp. gr. = 168° Tw. or 66° B.

Before chamber acid is thus concentrated, certain impurities have to be withdrawn. These accidental impurities are, in addition to traces of lead, copper, iron, lime, alumina, and sometimes selenium and thallium, oxides of nitrogen and arsenic. Nitrous acid may be removed from sulphurous acid by means of oxalic acid, which is decomposed into carbon dioxide and monoxide: $N_2O_3 + 3CO = 3CO_2 + 2N$.

The proportion of arsenic in sulphuric acid prepared from Sicilian sulphur is generally slight, but in that from pyrites and blende it is more considerable. For its removal there is used in many works sulphuretted hydrogen gas, which is prepared either from iron sulphide and dilute sulphuric acid (the residual lye being converted into copperas), or according to Sinding's proposal, by the action of generator gases upon pyrites at an elevated temperature. According to Hunt's process, sulphuretted hydrogen gas is caused to pass into vessels containing quartz stones, over which the arsenical acid is allowed to flow. The arsenic is thus thrown down as arsenic sulphide, and is separated from the sulphuric acid by means of a sand filter. At Oker, the acid to be purified is let flow into small precipitating pans and diluted down to 88° Tw. (sp. gr. 1·45). The pan is covered with a lead lid with a hydraulic joint, and the acid is heated to 75°, when sulphuretted hydrogen is introduced until the acid appears milky from the liberated sulphur. The acid is then clarified by standing for six hours, and is then passed through a small filter consisting of four double-bottomed sieves, between which are layers of asbestos. It is received in a cistern and kept for concentration. In the works at Chessy, near Lyons, barium sulphide is used for removing arsenic from chamber acid, to which it is added in the proportion of 0·2 to 0·3 per cent. Although a small quantity of acid is thus lost by combining with the barium to form sulphate, this process may be much recommended, as the sulphuretted hydrogen thus evolved from the barium sulphide is extremely effective.

* The amount of chamber room provided cannot well be less than 20 cubic feet per lb. of sulphur burnt.

† It is scarcely necessary to say that of the many proposals for dispensing with the lead-chambers none have proved successful.

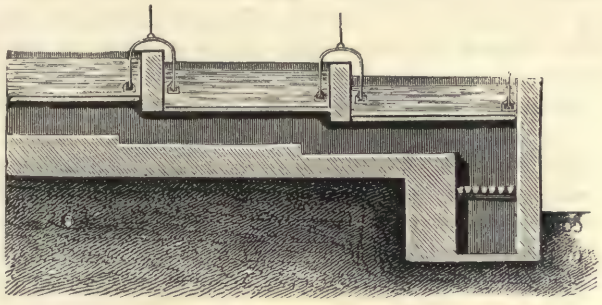
Sodium and barium thiosulphates have also been proposed for removing arsenious acid from the chamber acid. The precipitated arsenic sulphide is worked up as yellow arsenical glass.

As arsenic is almost exclusively present in sulphuric acid in the state of arsenious acid, it may be removed by the introduction of hydrochloric acid. There is formed arsenious chloride ($AsCl_3$), which boils at a temperature of 134°, and can thus be easily removed from sulphuric acid, as the latter does not boil below 325°–330°. If the arsenic occurs as arsenic acid, it must be previously reduced to the arsenious state. This is effected, according to Kupferschläger by means of a current of sulphurous acid; or according to Buchner by heating the chamber acid with a little charcoal, when sulphurous acid is also formed. The arsenious acid when formed is then removed, either by means of sulphuretted hydrogen, or of hydrochloric acid. The lead, indium, and thallium compounds present are removed by means of sulphuretted hydrogen as insoluble sulphides. Iron is found in the form of ferric sulphate in acid prepared from pyrites, especially in such as has been concentrated in the Glover tower.

Concentration of Sulphuric Acid.—When chamber acid is heated it begins to boil at 130°–135°, but the boiling-point continually rises until it reaches 338°. This last acid is the quality which is always obtained on the concentration of chamber acid. It contains 98 per cent. H_2SO_4, and on evaporation at the ordinary atmospheric pressure it gives off no more water.

Chamber acid is concentrated by heating in open lead pans up to 140°–146° Tw. (= 1·70 sp. gr.), then in vessels of platinum or glass up to 168° Tw. (= 66° B. or 1·84 sp. gr.).

Fig. 266.



Concentration in Leaden Pans.—Chamber acid does not begin to attack lead vessels until the concentration exceeds 148° Tw., so that it may safely be pushed up to 140°–146° Tw. in leaden pans. According to the experiments of Mallard, sulphuric acid at 140° to 160° Tw., if boiling, attacks lead, with the formation of sulphurous acid, lead sulphate, and sulphur ($SO_2 + 2Pb = S + 2PbO$). The lead pans are generally, though not universally, heated from below. A pan of this kind is shown in Fig. 266. As a rule several pans are arranged on steps, each successive pan, 40 to 50 centimetres in depth, being fixed from 3 to 7 centimetres lower than the previous one. Above the wall which separates every two pans, small syphons are suspended, the limbs of which stand in small cylindrical vessels. The syphons are always kept full. If they are immersed in the liquid over the partition wall, the acid runs from the one pan into the next lower one. The strength gradually increases in the pan.

The plates of lead, which are $1\frac{1}{2}$ centimetre in thickness, rest upon iron plates. From the last lead pan the sulphuric acid passes at once into the concentrating vessels of platinum or glass, in order there to be brought to 168° Tw.

In the pans of the second kind, the products of combustion sweep over the acid, which is contained in a lead pan in the side of the hearth of a reverberatory. The blackening of the acid thus occasioned is not objectionable if the acid is to be used in the alkali manufacture. At the Rhenania works, near Aachen, there was formerly used for concentrating the chamber acid a reverberatory, with a lead pan, 1·85 metre long, 1·25 metre wide, and 0·26 metre deep, and overhung for 15 centimetres by the fire bridge of masonry. The chamber acid flows laterally into the pan at the height

which is to be its level. At the bottom is a leaden syphon to draw off the concentrated acid. The acid, rendered stronger by the loss of water from its surface, sinks to the bottom and flows off through the syphon. The impurities introduced by the fire-gases float upon the surface.

In order to concentrate sulphuric acid with indirect steam, the evaporation is effected at Duisburg in wooden cisterns lined with lead, and of the length and breadth of 4 metres. On the bottom of each cistern lie two leaden worms, each 45 metres long, 0·03 metre inside diameter, and the sides of 0·007 metre in thickness, through which the steam flows whilst the cistern is filled with acid. In order that the condensed water may run off easily from the worms the bottom has the form of a truncated pyramid, and the cistern is in the middle, 0·6 metre, and at the sides 0·3 metre deep. Both ends of each worm are connected with the steam boiler and can be shut off with cocks. The steam boiler lies rather lower than the concentrating cisterns, which receive their steam from a pipe running off from the dome of the boiler. The pipes which convey away the steam from the concentration cistern incline towards the steam-space of the boiler, so as to permit a reflux of the condensed steam to the boiler. The cistern is filled with chamber acid of sp. gr. 1·5, and heated until it has risen to 1·7. The entire contents of the cistern are then transferred to a wooden tank lined with lead. In it lies a worm which the chamber acid must traverse on its way to the concentration cisterns, which are thus always fed with hot concentrated liquid. The pressure of steam in the boiler is three atmospheres, and, in an apparatus of the size given, 5000 kilos. of acid of sp. gr. 1·7 are obtained in twenty-four hours. The consumption of coal is 9 kilos. per 100 kilos. of concentrated acid. The consumption of lead is 2 kilos. per ton of sulphuric acid. It is advisable to place a screen of boards above the concentration cistern, to protect the workmen in case of the bursting of the pipes. Delplace makes the remark that at Stolberg the leaden steam-pipes are attacked at the point where they plunge into the liquid.* The dust which in time attaches itself to the pipes sucks up the acid by capillarity a few centimetres higher than its level in the pan; this acid is quickly concentrated by the heat and occasions an increased corrosion of the lead. The mischief is prevented by fixing, at the point where the pipe enters the end, a leaden bell of large diameter, opening upwards. Concentration by steam has been of late more common; no sulphuric acid is volatilised on account of the low temperature, and the process has the advantages of cleanliness, small consumption of fuel, and a decrease of labour.

The hot gases of the pyrites furnaces are often used for concentrating the chamber acid. To this end leaden pans are fixed upon or behind the furnaces, and the sulphurous acid is led from the furnaces into a leaden tower filled with hard burned bricks. This arrangement has the defect that, when the pans become leaky, the acid escaping ruins the furnaces. Such accidents, in fact, have frequently happened.

The concentration of the chamber acid by the hot sulphurous acid of the Glover tower has been already mentioned.

Completion of Concentration.—The acid obtained in the lead pans of a strength of 146° Tw. suffices for most purposes. If a more concentrated acid is required (168° Tw. = 1·847 sp. gr.), it is transferred to vessels of glass or platinum. It may be here remarked that the Baumé hydrometers used in many works are carelessly constructed. The point to which the instrument sinks in ordinary (?) sulphuric acid is marked as 66°, and the interval between that point and the point for water (0°) is divided into 66 parts. Samples of sulphuric acid which marked 67° on this instrument had a sp. gr. of only 1·80 and 1·81.†

* This is a very general phenomenon.

† It must be added that the tables for Baumé's hydrometer, as given in standard works, differ seriously. In Gmelin's *Handbook of Chemistry* (Cav. Soc. edition) 46° B. is given as equal

Concentration in glass vessels is very general. In Britain more than 70 per cent. of all the sulphuric acid is concentrated in glass vessels, the purchase and maintenance of which scarcely amount to half the interest on the cost of a platinum apparatus. Formerly there were used glass retorts of the ordinary shape, fixed to the number of ten in sand-baths in a galley furnace (Fig. 267). The necks have elongations which open into stoneware flasks to condense the escaping vapours. In the works of Chance & Co., of Oldbury, the glass vessel, *B* (Fig. 268), 85 centimetres high and

Fig. 267.

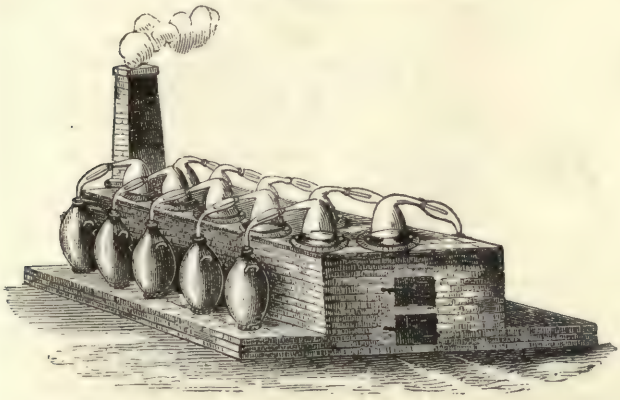
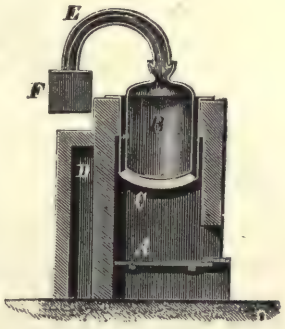


Fig. 268.



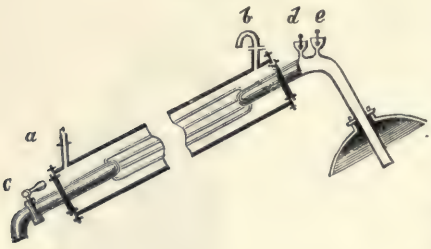
45 centimetres wide, holds 136 litres, and yields each time 87 litres (= 160 kilos.) of concentrated acid. *A* is the fire-box, and *C* the iron sand-bath, which has sand only at its bottom. The gases escape, through *D*, into the chimney. A glass elbow-tube, *E*, is in connection with the lead vessel, *F*, in which the distilled water is condensed. At the end of the process the pipes, *E*, are removed, and the acid is drawn off with a syphon without disturbing the vessels. During the work the upper part of the glass vessels is protected against chills and currents of air by covers of stoneware or of sheet-iron.

The glass vessels used in the chemical works at Muehlheim on the Rhine consist of the retort itself in the form of an ovoid body of 70–80 centimetres height and 40–50 centimetres diameter, and a capital which is like a laboratory retort without bottom. They are made of white, very thin glass, hold about 300 kilos. of acid, and cost about 38*s*. Of these retorts thirty-two stand in a row. Each is in an iron vessel filled with sand, into which the retort is embedded to about 10 centimetres from its neck. Each retort has a separate, direct fire, and is separated from the others by an iron screen 15 centimetres in height. The escaping gases from each pass in a common flue to the chimney. In front of the retorts there lies a thin leaden pipe for filling them, and before each single retort there branches off from this leaden pipe a smaller tube, which can be raised and lowered. When the retort is to be filled the lead tube is lowered into the neck and the acid flows in from a leaden pan at a higher level, in which the chamber acid has been previously concentrated. In this manner thirty-two retorts can be filled in half-an-hour. The emptying is effected whilst hot by means of glass syphons, which are "set" by suction from an air-pump. The arm is left loose in the neck of the retort. To prevent glass from coming in contact with glass, there are placed in the neck three or four small lead discs, upon which the arm rests. The arm of each retort enters a common lead tube about 20 centimetres in width, which lies along the retorts and is

either to 1·468 or to 1·456 sp. gr.; in Crookes's *Select Methods* 46° B. represents 1·434. Other varying values are to be found in other works. A further defect in Baumé's scale is that its indications cannot be simply recalculated into specific gravities. Hence, it would be well if Continental and American manufacturers would abandon this instrument.

connected with the chimney. It carries off the vapours from the evaporation. As some sulphuric acid escapes along with the water, the gases pass first through some coolers, consisting of large lead cylinders filled with coke and cooled by water. Here the so-called dropping acid is collected. All the retorts are in a building protected from draughts, whilst the fires are in an annex on the outside. In front of each retort there is a small glass window for observing the process and regulating the fire accordingly. Boiling begins in one to two hours; the entire process lasts eight to ten hours. The evaporation is continued until the acid becomes colourless—a certain sign that it has reached its full strength.

Fig. 269.



The platinum stills have a capital either of platinum or lead. The acid which distils over of sp. gr. 1·125 to 1·162 is either returned to the lead pans, or concentrated separately for the production of a purer acid, or used as it is. The cooling of the acid concentrated in the platinum still may be effected in several ways, *e.g.*, by the use of the Bréant syphon (Fig. 269) of platinum. Its limb, situate outside the still, is 5 metres long, and is fitted with a copper tube 15 centimetres in width and 4 metres in length; it is filled with cold water at *a*, whilst the heated water flows off at *b*. To increase the surface of the syphon, its main pipe is divided into four narrow tubes. The syphon is set by closing the cock at *c*, and then pouring in sulphuric acid at the ball valves at *d* and *e* to form a tight hydraulic joint; the

Fig. 270.

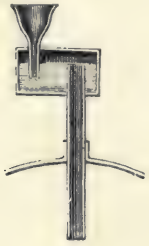


Fig. 271.

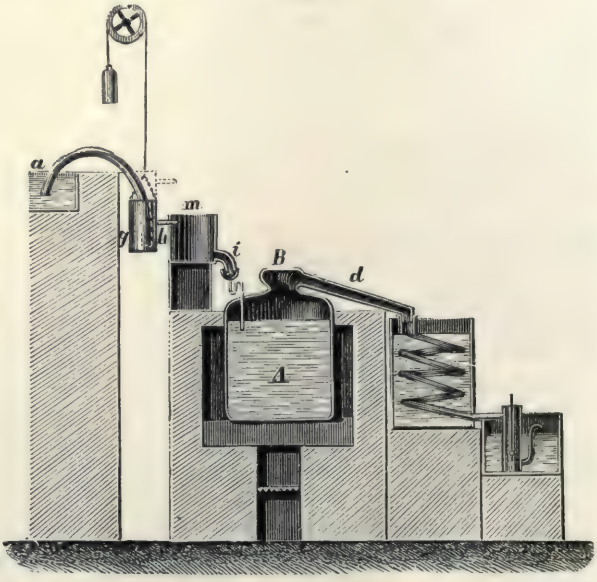
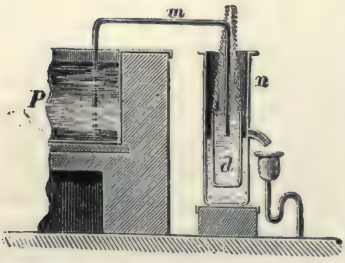


Fig. 272.

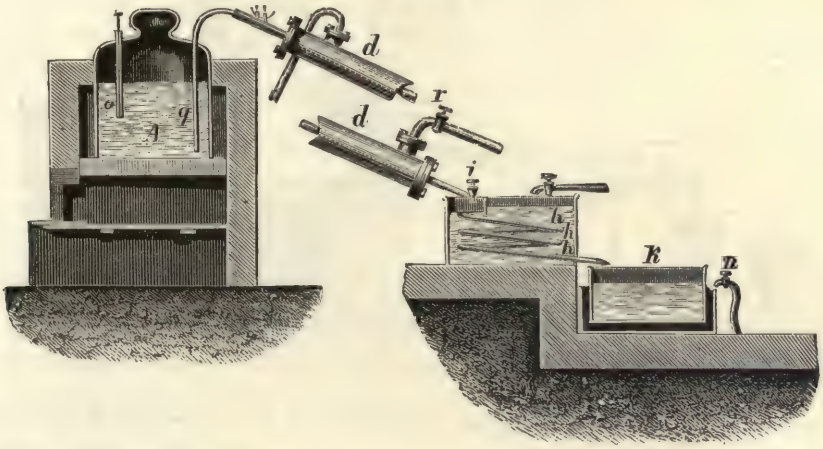


cock, *c*, is opened and the acid flows out. If it were necessary to delay drawing off the acid until cold, time would be lost and the still could not effect a quantity of work commensurate with its high price.

The arrangement of a platinum still with a platinum capital is shown in Figs. 270, 271, 272, and 273. The platinum tube, *d*, connects the capital, *B*, with a cooling worm of lead lying in water. The S-tube of platinum, *i*, with its funnel, has sometimes the shape as in Fig. 270. A cylindrical leaden vessel, *g*, is provided with an exit tube, *h*,

and the similar leaden vessel, *m*, has at its side a slit, so that the tube, *h*, can move in it up and down when the cylinder, *g*, is lifted up or let down. A filled leaden syphon connects *a* with *g*. If the cylinder, *g*, is drawn up as high as it is shown by the dotted lines in Fig. 271, the syphon ceases flowing, but if it is let down the acid of the pan flows through the funnel, *i*, into the pan, *A*. Still more simple is the arrangement shown in Fig. 272. A syphon, *m*, dips in the pan, *P*, and on the other side into the beaked vessel, *n*. In proportion as the small cylinder, *d*, suspended to the chain is raised or lowered, the outflow of the acid is regulated or stopped entirely. Fig. 273 shows the apparatus

Fig. 273.

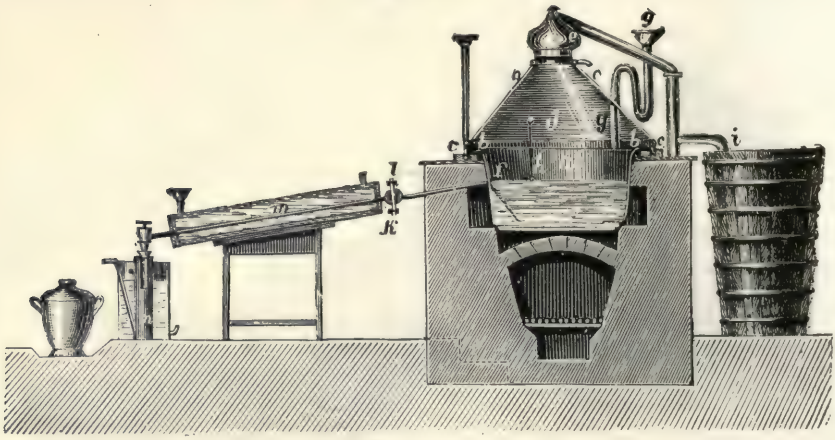


in section at right angles to Fig. 271. In the platinum pan, *A*, there is a perforated tube, *o*, of platinum, in which is a float of glass showing the level of the acid in the pan. The long limb of the platinum syphon, *d*, lies in a wide iron tube supplied with cold water. The syphon, generally of Bréant's design, ends in a platinum cock, *i*. The pan stands on a disc of fire-clay with perforators, into which the flame penetrates and plays round the retort. The specific gravity of the acid which drops off through the pipe of the capital, *d* (Fig. 271), shows the progress of the work. In the Oker Works on the Harz, a strength of 20° B. here is understood to indicate that the acid in the platinum pan has become 66° B. = 168° Tw., and is fit to be drawn off. It then flows for refrigeration through the cooling apparatus, *d* and *h*, into the leaden vessel, *k*, which is surrounded with cold water, from *n*. The acid when sufficiently cooled is run into the well-known carboys, holding each about 100 kilos., which are placed in wicker baskets packed with straw, and closed by a clay stopper.

Latterly, platinum apparatus with a leaden capital are coming into use. The apparatus of Johnson, Matthey & Co. (Fig. 274) consists of a platinum body, 0·75 metre wide and 0·50 metre in height; its upper margin, *b*, is bent over for 5 centimetres. This margin bending outwards forms, with channel of platinum resting on the wall built round the platinum body, a hydraulic joint, which is placed for the protection of the platinum in a channel of iron or lead. In this channel, which is about 15 centimetres wide, there rests the conical capital of strong lead, *d*, which covers the platinum vessel as with a lid, and on the upper part of which is soldered a low cap, *e*, with a strongly sloping tube, both of lead. The syphon for drawing off the concentrated acid is attached to the side of the body at *f*, the level of the acid provided for, so that when the acid reaches this height it runs off spontaneously. To the leaden cap are soldered the inflow pipe, *g*, for the acid to be concentrated, and the arrangement, *h*, for the gauging glass. The pipe sloping down from the cap is connected with the cooling worm, *i*, in order to carry back to the cooler any vapours which might

escape. The syphon for drawing off the concentrated acid projects out of *k*, and is connected with the cooling tube, *m*, 1½ metre in length, by means of the ball-joint, *l*. Hence the acid finally flows through a very efficient pot-cooler, *n*, which makes it possible to run the acid at once into carboys. To keep the leaden cap cool and prevent it from sinking in on account of the great heat of the boiling acid, it is surrounded with a cylindrical screen, by which the cap itself becomes a kind of evaporating pan, which,

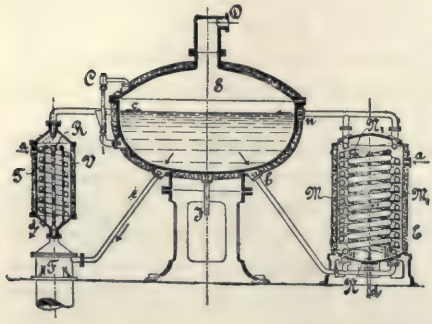
Fig. 274.



when kept constantly full of chamber acid, effects the double purpose of cooling and concentration.

The platinum-lead concentrator of Faure and Kessler aims at high efficiency in the concentration of the acid, combined with a great economy of platinum. It consists of a very large, but shallow, platinum pan, or of several flat pans connected together, and heated from below by a direct fire. The depth of the acid is small. Over the platinum pan is a covering of lead, the outside of which is kept cool by a stream of water. On the inside the acid-vapours ascending from the platinum pans are liquefied, and led outwards by a channel. The sulphuric acid flows in a continuous stream from the back to the front, and is drawn off in the ordinary manner by a platinum syphon as acid of 168° Tw.

Fig. 275.



As far back as 1844, Kuhlmann recommended the use of a reduced atmospheric pressure. Latterly this procedure has been repeatedly applied. In the arrangement proposed by the International Vacuum Ice-Machine Company of Berlin, the pan, *S* (Fig. 275), made of hard lead, is surrounded with a bad conductor of heat, and fitted with a gauge-glass, *C*. Into the steam-vessel, *E*, made of iron or copper plates, there are introduced the leaden worms, *M*, M_1, traversed by the acid, and resting on the inner supports, *N*, N_1. The steam for heating enters at *a*, whilst the steam-water flows off at *d*. The acid to be concentrated passes through the exchange apparatus, *F*, through the worm, *T* (surrounded by steam), of the heater, *V*, and enters the pan at *c*. The acid, which has become colder and heavier by the removal of the watery vapours, goes in the direction of the arrows, *b*, to the heater, *E*, placed lower than the pan. Here it is

heated anew, and makes a continual circuit, as in a common water-heating apparatus. The watery vapour is drawn off at *D*, and the concentrated acid is let off at *J*.

The ordinary sulphur acid of commerce contains 93 to 96 per cent. of the so-called monohydrate, H_2SO_4. Exceptionally, a stronger acid of 97 or, at the utmost, 98 per cent. is obtained by further evaporation in glass or platinum vessels; stronger acid cannot be obtained in this manner, as the monohydrate is dissociated even at a moderate temperature, leaving acid of 98 to 98·5 per cent. G. Lunge has observed that, by refrigerating 98 per cent. acid at a little below 0°, monohydrate can be made to crystallise out on an industrial scale, but that the same result can be obtained with acids of 97 or even 96 per cent. by cooling down to − 10°, if the occurrence of superfusion is obviated by dropping in a few crystals of the monohydrate. A small quantity of crystals of monohydrate are first prepared by freezing at −10° a 98 per cent. acid (obtained by firing ordinary or fuming acid). A sulphuric acid at 96 to 97 per cent. is next cooled down to at least 0°, then a few crystals of the monohydrate are thrown in, and the whole is further cooled with stirring until the formation of crystals is completed. The mother liquor is then removed by draining, pressing, &c., not letting the temperature rise above 0°.

Of the many modern proposals for manufacturing sulphuric acid in novel manners the following may be mentioned.

Hahner oxidises sulphurous acid by chlorine in presence of watery vapour:

$$SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl.$$

The chlorine is obtained from the hydrochloric acid produced in the alkali manufacture (Deacon's process). If the sulphuric acid is to serve for the decomposition of common salt it does not need to be purified from hydrochloric acid. Gypsum, $CaSO_4.2H_2O$, has been repeatedly considered as a source of sulphuric acid, and various methods have been proposed to obtain sulphuric acid from gypsum and similar sulphates, without any such proposal having been carried into successful execution. Tilghman places pieces of gypsum in an upright earthen cylinder lined with magnesite. The charge is then heated to full redness, and the gaseous products of decomposition, O, SO_2, and H_2SO_4, are conveyed through the bottom and the top to the lead chambers. Quicklime is said to be left in the cylinder. Epsomite may be treated in the same manner.

Seckendorff introduced powdered gypsum and lead chloride into stone tanks along with a large quantity of water heated to 50°–60°. The mixture must be well stirred. Both salts are rapidly decomposed:

$$CaSO_4 + PbCl_2 = CaCl_2 + PbSO_4.$$

The calcium chloride remains in solution whilst the lead sulphate forms a precipitate, which is filtered off and treated with hydrochloric acid in excess:

$$PbSO_4 + 2HCl = PbCl_2 + H_2SO_4.$$

The mixture is stirred and heated to 60°, when lead chloride collects at the bottom, and the sulphuric acid remains in solution, and is concentrated in the usual manner. The lead chloride serves for the decomposition of fresh quantities of calcium sulphate. If hydrochloric acid is passed over calcium sulphate at a red heat, sulphuric acid escapes and calcium chloride remains:

$$CaSO_4 + 2HCl = H_2SO_4 + CaCl_2.$$

According to Scheurer Kestner, if 2 parts calcium sulphate are heated to bright redness with 1 part ferric oxide, all the sulphuric acid is expelled. Sulphuric anhydride escapes first and afterwards sulphurous acid and oxygen. The behaviour of magnesium sulphate is similar.

PROPERTIES OF SULPHURIC ACID.

The most highly concentrated sulphuric acid, of the formula H_2SO_4, has the sp. gr. 1·857 (J. Kolb), 1·854 (Marignac), 1·8384 (Lunge and Naef). When pure it is a perfectly colourless liquid, which, however, is commonly coloured yellowish or brownish, owing to the accidental presence of particles of organic dust. It is thick and oily, destroys many organic bodies with liberation of carbon, does not fume in the air, and is so hygroscopic that it gradually absorbs 15 times its own volume of water. If mixed with water, great quantities of heat are liberated. Of all the volatile acids it has the greatest affinity for bases, and, on heating, it expels all other volatile acids from their salts. But at a red heat sulphuric acid is expelled from its salts (partly decomposed into sulphur dioxide, oxygen, and water) by silicic, boric, or phosphoric acid. The boiling-point of the most concentrated acid is 338°.

Per cent. H_2SO_4.	Specific Gravity.	Specific Gravity.	Baumé.
90	1·8185	1·8202	65·1°
91	1·8241	1·8254	65·4
92	1·8294	1·8306	65·6
93	1·8339	1·8346	65·8
94	1·8372	1·8374	65·9
95	1·8390	1·8397	66·0
96	1·8406		
97	1·8410		
97·75	—	1·8468	66·2
98	1·8412		
99	1·8403		
100·00	1·8384		

Specific Gravities of Sulphuric Acid at 15° (Kolb).

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	100 Parts by Weight correspond to per Cents.		1 Litre contains Kilos. of Pure Acid.	
			SO_3.	H_2SO_4.	SO_3.	H_2SO_4.
1·000	0	—	0·7	0·9	0·007	0·009
1·014	2	2·8	2·3	2·8	0·023	0·028
1·029	4	5·8	3·9	4·8	0·040	0·049
1·045	6	9·0	5·6	6·8	0·059	0·071
1·060	8	12·0	7·2	8·8	0·076	0·093
1·075	10	15·0	8·8	10·8	0·095	0·116
1·091	12	18·2	10·6	13·0	0·116	0·142
1·108	14	21·6	12·4	15·2	0·137	0·168
1·125	16	25·0	14·1	17·3	0·159	0·195
1·142	18	28·4	16·0	19·6	0·183	0·224
1·162	20	32·4	18·0	22·2	0·209	0·258
1·180	22	36·0	20·0	24·5	0·236	0·289
1·200	24	40·0	22·1	27·1	0·265	0·325
1·220	26	44·0	24·2	29·6	0·295	0·361
1·241	28	48·2	26·3	32·2	0·326	0·400
1·263	30	52·6	28·3	34·7	0·357	0·438
1·285	32	57·0	30·5	37·4	0·392	0·481
1·308	34	61·6	32·8	40·2	0·429	0·526
1·332	36	66·4	35·1	43·0	0·468	0·573
1·357	38	71·4	37·2	45·5	0·505	0·617
1·383	40	76·6	39·5	48·3	0·546	0·668
1·410	42	82·0	41·8	51·2	0·589	0·722
1·438	44	87·6	44·1	54·0	0·634	0·777
1·468	46	93·6	46·4	56·9	0·681	0·835

Kohlrausch has shown that sulphuric acid has its maximum density below its highest concentration.

Applications.—The applications of sulphuric acid are extremely extensive and manifold; *e.g.*, in the preparation of many acids (nitric, hydrochloric, sulphurous, carbonic,

tartaric, citric, stearic, palmitic, and oleic), for producing acid calcium phosphate as a manure for the production of chlorine, of stearine candles (decomposition of lime soaps), of phosphorus (by decomposing bone-earth), for making salt-cake in the alkali-manufacture, the production of potassium sulphate (from the potassium chloride or carnallite), of ammonium sulphate, alum, iron and copper vitriols, baryta white, hydrogen gas, nitro-glycerine, gun-cotton, picric acid, in separating gold from silver, de-silvering black-coppers, for refining rape oil, petroleum, and paraffine, obtaining garancine or other madder products, for producing the sulphonic acids of the tar-colours, for manufacturing glucose, parchment paper, shoe-blacking, as a disinfectant, for desiccating confined air (*e.g.*, for glue), for drying the chlorine obtained in the Deacon process, for cleaning sheet-iron to be tinned, &c.

POTASSIUM SALTS.

Potassium is found widely diffused both in the mineral kingdom and in organic nature. The sources of potash available for technical purposes are at present the following :—

A. Inorganic sources.
1. Natural salts, carnallite, sylvine, kainite, and schœnite.
2. Felspar, and similar rocks.
3. Sea-water, and the mother liquor of salt-works.
4. Native saltpetre.

B. Organic sources.
5. Ash of plants.
6. Residue from beetroot treacle.
7. Seaweeds ; a bye-product of the iodine manufacture.
8. The suint from raw wool.

Of these sources the most important at present are the deposits of alkaline salts. They are supposed to have been formed by the gradual drying up of salt lakes or arms of the sea. Similar phenomena are at present gradually taking place in Central Asia. The more soluble salts, those of potassium and magnesium, would remain in solution longer than sodium chloride, and would thus be in danger of being swept away by intermediate geological changes, inundations, &c. Hence of the many and vast saline beds in the earth, many are totally free from potassium salts, which in North Germany have been accidentally preserved. At Kalucz in Hungary, and on the southern slopes of the Himalaya, similar deposits occur.

Potassa Salts from the Stassfurt Salt Minerals.—I. The very abundant salt-rocks near Stassfurt in Prussia, and Kalucz in Hungary, chiefly yield carnallite, sylvine (ClK), and kainite, a compound of sulphate of potassa and magnesia with chloride of magnesium. Carnallite, so named in honour of Carnall, a Prussian mining engineer, consists, in 100 parts, leaving the bromide out of the question, of—

Potassium chloride	27
Magnesium chloride	34
Water	39
	100

Formula—$KCl_2,Mg\begin{cases}Cl_2\\Br_2\end{cases}+6H_2O$. This salt is applied in the manufacture of—

a. Potassium chloride.
β. „ sulphate.
γ. „ carbonate.

a. Preparation of Potassium Chloride.—According to the process originally patented (1861) by Mr. A. Frank, the abraum salts are ignited in a reverberatory furnace, with or without the aid of a current of steam, and next lixiviated with water, the resulting liquor yielding chloride of potassium. The *rationale* of this process is :—
1. That the carnallite of the abraum salts is separated by the action of the water into

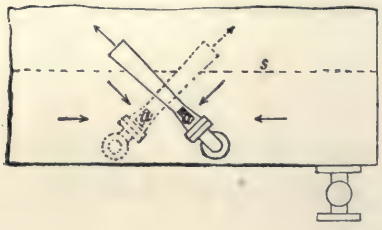
chloride of potassium and chloride of magnesium. 2. The latter salt on being ignited in a current of steam is decomposed into hydrochloric acid, which escapes, and magnesia, which is practically insoluble in water, and which consequently remains. This process is not found to answer well on the large scale, because the abraum salts contain other chlorides, the chloride of sodium and tachydrite, by the presence of which the decomposition of the carnallite is hindered. Dr. Grüneberg, therefore, suggested that the abraum salts should be first mechanically purified, that is to say, the different components of the abraum salts should be separated from each other according to their varying specific gravity, which for—

Carnallite	is = 1·618
Chloride of sodium	is = 2·200
Kieserite	is = 2·517

The abraum salt having been ground to a coarse powder is passed through sieves, and treated as minerals are in metallurgical processes, with the difference that, instead of water, which of course would dissolve the salts, a thoroughly concentrated solution of chloride of magnesium is applied, this solution not acting upon the salts, and being, moreover, obtained as a bye-product in enormously large quantities. The above-mentioned salts settle in layers according to their densities, the carnallite forming the upper, and the kieserite the lowest layer. The carnallite is at once applied to the preparation of chloride of potassium; the middle layer of common salt is so free from other foreign salts as to be fit for domestic use; the kieserite, after having been washed with cold water to remove any adhering chloride of sodium, is applied to the manufacture of sulphate of potassa, to be presently described. However, the greater number of manufacturers at Stassfurt prefer another plan, applying the five following operations to the abraum salts as delivered from the salt quarries:—1. Lixiviation of the carnallite with a limited quantity of hot water, sufficient to dissolve the chlorides of potassium and magnesium, leaving the bulk of the common salt and magnesium sulphate. 2. Crystallising the chloride of potassium by artificially freezing. 3. Evaporating and cooling the mother liquor to produce a second yield of crystallised chloride of potassium. 4. Again evaporating and cooling the mother liquor, which yields the double salt of the chlorides of potassium and magnesium, or artificial carnallite, which is next treated in the same manner as the native salt. 5. Washing, drying, and packing the chloride of potassium.

According to Dupré, ejection apparatus (Fig. 276) are used, so arranged that their suction openings, *a*, are in connection with the space beneath the sieve flooring, *s*, whilst the ejection openings are connected with the space above this flooring. At the same time, the direction of the apparatus is such as to produce an intense circulation of the liquid and the saline particles.

Fig. 276.

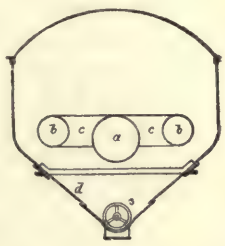


The hot solution obtained, of sp. gr. 1·32, is allowed to stand in separate vessels to deposit the suspended particles (of kieserite and clay), and then it is let flow into iron crystallising tanks, in which, after cooling for two to three days, a mixture of potassium and sodium chlorides crystallises out. In some works the crude saline solution is diluted with water, whereby the separation of sodium chloride is diminished and a crystallisation of almost pure potassium chloride is effected. In order to obtain the potassium chloride still remaining in the mother liquor, the latter is evaporated down to such a concentration that the potassium chloride separates almost entirely out in the form of carnallite, and only 1 per cent. is left in solution. The artificial carnallite is dissolved in hot

water, and, as it cools, a second crystallisation of potassium chloride is obtained. The potassium chloride obtained from both crystallisations is washed with water at common temperatures to remove magnesium chloride, and in part sodium chloride; it is dried in a calcining furnace or on kilns heated by steam. The mother liquor from the second crystallisation, and the washings containing potassium, sodium, and magnesium chlorides, are used for dissolving the crude salt.

The pans for evaporating the mother liquor in the manufacture of potassium chloride have three flame tubes, the middle one, *a* (Fig. 277), having double the section of the two side tubes, *b*. The flame strikes first backwards through the middle tube and then forwards through the side tubes. Hitherto the flame tubes were rivetted to both cheeks of the pan, which easily occasioned a strain and a loosening of the joints. For the ready removal of the sodium chloride, which separates out on the evaporation of the mother liquor, the bottom of the pan slopes towards the middle, *d*, and the lowest point is provided with a helix, *s*. By its rotation the salt is removed which has been deposited in the lowest part of the pan.

Fig. 277.



Of the potassium chloride present in the crude salt, 75 to 85 per cent. is obtained; the rest is lost in the various residues. The proportion of potassium chloride in the muddy settlings is sometimes considerable, so that the salt calcined in some works and sold for manure may contain 18 to 24 per cent. potassium chloride. Supposing the loss in the manufacture to be 20 per cent., then 625 kilos. crude salt at 16 per cent. are needed for the production of 100 kilos. potassium chloride at 80 per cent. For the daily manipulation of 50 tons raw salt a space of 350 cubic metres is needed for crystallising, or for a daily turn-over of 3500 tons a total of 24,500 cubic metres.

Of the potassium chloride 80 per cent. is used in the manufacture of potash saltpetre, whilst for the preparation of potash a pure product, as free as possible from sodium chloride, is needed.

As bye-products, kieserite and sodium sulphate are obtained from the residues. The former is produced in the simplest manner, by dissolving the sodium chloride found, when the sparingly soluble kieserite is split up and deposits as a fine mud; this takes up water and hardens in a few hours, and is sold in blocks weighing 25 kilos. From a part of the kieserite pure magnesium sulphate is obtained by solution and crystallisation.

The manufacture of Glauber's salt (sodium sulphate) is carried on only in winter. It depends on mutual decomposition of sodium chloride and magnesium sulphate in aqueous solutions at temperatures below 0°. To this end, the total residue is dissolved in water; the concentrated lye obtained after it has become clear is exposed in flat exposed wooden troughs to the cold of winter. The crystallisation is often effected in a single night. In this manner about 10,000 tons sulphate are produced yearly. After the introduction of freezing machines the output will be decidedly greater.

The conversion of potassium chloride into potassium sulphate by Glauber's salt, which has been repeatedly tried, has not been found practicable on the large scale, as the two sulphates have a great tendency to form a double salt. At present large quantities of potassium sulphate are prepared by means of sulphuric acid in a manner quite analogous to the Leblanc soda process and with the same apparatus and furnaces.

Grüneberg and Schmidtborn allowed a hot solution of potassium chloride and schœnite to crystallise. The result was potassium chloride and carnallite, which are separated by crystallisation.

Müller fuses equivalent quantities of potassium chloride, magnesium sulphate, and iron oxide. The potassium sulphate is separated by lixiviation.

Kainite.—In the interval between 1878–1880, sixteen processes were patented for the production of potassium magnesium sulphate, of which only three have been worked on the large scale. The United Chemical Works of Leopoldshall work on the Borsche and Brünjes process, the Stassfurt Chemical Works on that of Dupré and Hake, and the new Stassfurt Works under the patent of H. Precht. Borsche and Brünjes treat the kainite with a cold saturated solution of kainite at 80°; on cooling, potassium-magnesium sulphate crystallises. Dupré and Hake use in a similar manner a concentrated solution of magnesium sulphate, whilst Precht heats the kainite with water or brine to 120° to 150° under pressure. In this manner 3 tons of coarsely powdered kainite are decomposed in about thirty minutes, the potassium-magnesium sulphate being converted into an exceedingly fine crystalline powder, $K_2SO_4.2MgSO_4.H_2O$. For dissolving there is used a saline solution saturated for sodium chloride, which may contain other of the salts occurring in kainite. The proportions are chosen so that sodium chloride and the new double salt remain undissolved, whilst potassium and magnesium chlorides remain in solution. According to the nature of the saline solution, the decomposition takes place according to one of the two following equations:—

$$3(K_2SO_4,MgSO_4,MgCl_2,6H_2O) = 2(K_2SO_4,2MgSO_4,H_2O) + 2KCl + 2MgCl_2 + xH_2O, \text{ or}$$
$$2(K_2SO_4,MgSO_4,MgCl_2,6H_2O) = K_2SO_4,2MgSO_4,H_2O + 2MgCl_2 + K_2SO_4.$$

The transformation ensues according to the former equation if the saline solution contains, along with sodium-chloride potassium, magnesium sulphate and magnesium chloride, but chiefly according to the second, when it consists of a saturated solution of magnesium chloride. Experience in manufacturing has shown that the new salt is precipitated so completely from the decomposition-lye, that this on cooling only allows potassium chloride to separate and does not contain more than 2·4 per cent. magnesium sulphate. In contact with cold water it is resolved into schœnite and epsoms. From the hot aqueous solution schœnite crystallises out on cooling, whilst the excess of magnesium sulphate remains in solution. If a solution of potassium chloride is taken as a solvent, we find conversion into schœnite and magnesium chloride.

The potassium-magnesium sulphate, with 50 per cent. potassium sulphate and 3 per cent. chloride, is in great demand both in agriculture and manufactures, and perhaps from this cause its further treatment for pure potassium sulphate is not yet carried out.

The utilisation of the abundant lyes of potassium chloride is still an unsolved problem. A small portion is evaporated down, and the melted magnesium chloride is sold; from a larger portion the 0·2 per cent. of bromine present is separated before it is let run into the streams. At present about one-third of the final lye is thus treated with an annual yield of 300 tons.

Production of Potassium Carbonate.—Numerous proposals have been made for the most advantageous conversion of potassium chloride and sulphate into potash. The only process which has been practically carried out is an imitation of the Leblanc soda process, first applied to the production of potash by Grüneberg (1861). Large quantities of excellent potash have been made by Forster and Grüneberg, at Kalk, near Cologne, at the Buckau Works, near Magdeburg, and at Stassfurt, on the Leblanc process. Everything is carried on as for soda, save that in the black-ash process high temperatures must be more carefully avoided. If the coal used for reduction is rich in nitrogen, potassium ferrocyanide is produced. On evaporating the carbonated lye to 98° Tw., the ferrocyanide separates out with the undecomposed sulphate still contained in the lyes, and can be extracted from the salt by lixiviation with hot water; a second re-crystallisation converts the product into a fine commercial sample.

The products prepared at Buckau contained (1879)—

K_2CO_3	97·30 per cent.
Na_2CO_3	0·29 „
K_2SO_4	0·49 „
KCl	1·23 „
Moisture	0·69 „

According to another process, potassium sulphate containing schœnite is ignited with chalk and small coal, and the mass lixiviated with water. Potash dissolves, and calcium sulphide remains, from which the sulphur is recovered according to the processes of Schaffner and Mond. The presence of a certain quantity of schœnite and magnesium sulphate in potassium sulphate which is intended for the manufacture of potash is advantageous, since the crude potash is thus rendered lighter and more porous, and it is consequently easier to lixiviate than crude potash made from a pure potassium sulphate.

R. Engel mixes a solution of potassium chloride with magnesium carbonate and saturates with carbon dioxide, when the double potassium-magnesium bicarbonate separates out. When separated from the lye of magnesium chloride, this precipitate is heated either alone or along with water, when it is resolved into magnesium carbonate and potassium carbonate—

$$2MgKH(CO_3)_2 = 2MgCO_3 + K_2CO_3 + H_2O + CO_2$$

The potassium carbonate is extracted in the water. Magnesium carbonate and carbon dioxide go back. The process has recently been given up.

Experiments to obtain potassium carbonates by the ammonia process have hitherto had little success.

For the preparation of potassium carbonate, G. Borsche and F. Brünjes introduce carbonic acid and ammonia, or ammonium carbonate, into the solution of a magnesium salt which holds in suspension magnesia or magnesium carbonate, on which the double ammonium-magnesium carbonate (containing all the magnesia in solution) is separated out after some time. This double carbonate is mixed with about an equivalent quantity of potassium chloride or sulphate, an excess being of advantage, and with water, in order to bring the above salts into solution. Into this mixture is passed carbonic acid, or carbonic acid and ammonia, when the transformation into potassium magnesium is promoted, though it certainly takes place without the introduction of carbonic acid and ammonia. This preparation of ammonium-magnesium carbonate, and its transformation into potassium-magnesium carbonate can be combined by introducing, firstly, ammonium carbonate and carbonic acid—*e.g.*, into a solution of carnallite, or into a solution of potassium magnesium sulphate, or into suspended magnesia or magnesium carbonate, adding after some time potassium chloride, and then again carbonic acid. They thus obtain crystals of the triclinic system, containing potassium-magnesium carbonate. The potassium-magnesium carbonate is decomposed into potassium carbonate and magnesium carbonate by digestion with water. The magnesium carbonate returns to the process. This method is about to be introduced on a large scale.

The production of potassium salts from felspar is at present of no importance.

In order to obtain salts of potassium from sea-water, especially from the Mediterranean, the last mother liquors are concentrated by evaporation, and mixed with magnesium chloride, so that carnallite crystallises out.*

Salts of Potassium from the Ashes of Plants.—The residue left from the ignition of the organic matter, or wood, as it is usually termed, of plants contains those mineral substances which the plant has taken from the soil, chiefly potassa, soda, lime, magnesia, small quantities of the protoxides of iron and manganese, combined with phosphoric, sulphuric, silicic, and carbonic acids, and also with the haloids. These combinations are

* It has been proposed to apply this process to the water of the Dead Sea.

not, however, the same as those existing in the living plant, because the high temperature of the ignition has the effect of changing the affinities. Plants growing near the sea generally contain large quantities of soda, while those inland contain generally more potassa. The quantity of ash varies not only for different kinds of plants, but for various parts of the same plant: very succulent plants and the most succulent parts of others generally yield the largest quantity of ash; herbs yield more ash than shrubs, shrubs more than trees, and the leaves and bark of the latter more than the wood. It is evident that the inorganic matter, chiefly alkaline salts, being contained in the juice of plants in a soluble state, the quantity must of necessity be greatest in the juicy and succulent parts.

Dr. Bottger found the ash of beech wood to contain—

21·27 per cent. of soluble salts,
78·73 „ of insoluble salts.

The soluble salts were found to be—

Potassium carbonate	15·40 per cent.
„ sulphate	2·27 „
Sodium carbonate	3·40 „
„ chloride	0·20 „
	21·27 „

The value of an ash for the manufacture of potash is chiefly dependent, in the first place, upon the quantity of potassic carbonate it will yield, upon the abundance of the wood or other vegetable product, and the cost of labour. The under-mentioned woods yield on the average, for 1000 parts, the following quantities of potash:—

Pine	0·45	Beech bark	6·00
Poplar	0·75	Dried ferns	6·26
Beech	1·45	Stems of maize (Indian corn)	17·50
Oak	1·53	Bean straw	20·00
Box wood	2·26	Sunflower stems	20·00
Willow	2·85	Nettles	25·03
Elm	3·90	Vetch straw	27·50
Wheat straw	3·90	Thistles	35·37
Bark from oak-knots	4·20	Dried wheat plant previous to blooming	47·00
Cotton-grass (*Eriophorum vaginatum*)	5·00	Wormwood	73·00
Rushes	5·08	Fumitory	79·00
Vine wood	5·50		
Barley straw	5·80		

According to M. Hoess, 1000 parts of the following kinds of wood yield—

	Ash.	Potash.		Ash.	Potash.
Pine	3·40	0·45	Willow	28·0	2·85
Beech	5·80	1·27	Vine	34·0	5·50
Ash	12·20	0·74	Dried ferns	36·4	4·25
Oak	13·50	1.50	Wormwood	97·4	73·00
Elm	25·50	3·90	Fumitory	219·0	79·90

The preparation of potash from vegetable matter is effected in three operations, viz.:—

(*a*) The lixiviation of the ash.
(*b*) The boiling down of the crude liquor.
(*c*) The calcination of the crude potash.

The combustion of the vegetable matter should be so conducted as to prevent its becoming too violent and giving rise to the volatilisation of some of the reduced potassa salt; nor should too strong a current of air be admitted, for fear of the ash being mechanically carried off. A distinction is made abroad—no potash from wood or other

vegetable matter being produced in the United Kingdom, nor wood used as fuel in sufficient quantities to yield ash for the preparation of potash—between the ash obtained by the combustion of the refuse wood of forests and the ash from wood used as fuel, the former being termed *forest-* and the latter *fuel*-ash. As ash from other fuel than wood may be mixed with fuel-ash, a sample may be roughly tested by lixiviation, and the density of the liquor taken by the areometer, the higher the specific gravity the larger the quantity of soluble salts. Formerly the forest-ash was purposely prepared and sold to potash-boilers. There is still known in Eastern Prussia and Sweden a material termed *okras* or *ochras*, holding a position intermediate between crude ash and potash.

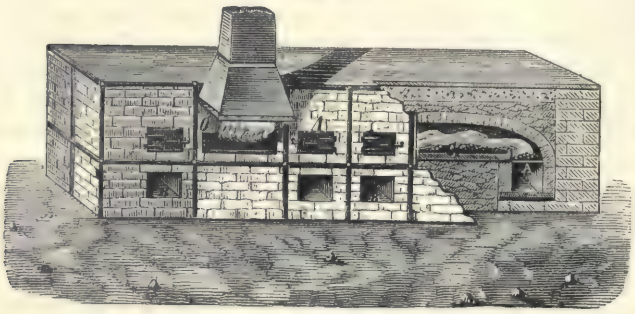
(*a*) The lixiviation of the ash effects the separation of the soluble from the insoluble saline matter, the former amounting to about 25 to 30 per cent. of the entire weight of the ash. The operation is carried on in wooden vessels shaped like an inverted truncated cone, and provided with a perforated false bottom, which is covered with straw; in the real bottom a tap is fixed for removing the liquor. If the lixiviation is systematically carried on, several of these vessels are placed together, forming what is termed a battery, and under each a tank to receive the liquor. The ash to be lixiviated is first sifted from the coarse particles of charcoal, next put into a small square water-tight wooden box, and thoroughly saturated with water for at least twenty-four hours. By this proceeding the lixiviation is greatly assisted, and the potassium silicate to some extent decomposed by the action of the carbonic acid of the atmosphere. The next step is to transfer the wet ash to the lixiviation vessel, care being taken to press it tightly down on to the false bottom; cold water is then poured in, until the liquor begins to run off at the taps left open for that purpose. The liquor which runs off, after the water has remained some little time in contact with the ash, is found to contain about 30 per cent. of soluble salts, afterwards decreasing to about 10 per cent., when hot water is employed to compete the lixiviation. The insoluble residue left in the lixiviation-tub is of value as a manure, on account of the phosphate of lime it contains, and is also used in making green bottle-glass, and for building up saltpetre-beds.

(*b*) Boiling down the liquor. The liquor obtained by lixiviation is of a brown colour, owing to organic matter, humine or ulmine, which the potassium carbonate has dissolved from the small chips of imperfectly burnt charcoal. The evaporation is carried on in large shallow iron pans, fresh liquor being from time to time added, and the operation continued until a sample of the hot concentrated liquor exhibits on cooling a crystalline solid mass. When this point is reached the fire is gradually extinguished, and as soon as the contents of the pan are sufficiently cold to handle, the solid salt mass is broken up; its colour is a deep brown. This crude product, containing about 6 per cent. water, is known in the trade as crude, or lump-potash. It is evident that this method of boiling down may cause considerable damage to the iron pans; therefore in many instances the operation is conducted in a somewhat different manner. The liquid is kept stirred with iron rakes, and the salt, instead of forming a hard solid mass, is obtained as a granular powder, containing upwards of 12 per cent. water. Some manufacturers first separate the potassium sulphate, which, being less soluble, crystallises before the carbonate, a deliquescent salt, is separated from the liquor; in most cases, however, this operation is only carried on where the potassium sulphate is required for alum-making. The pearl-ash or potash of commerce almost invariably contains a large quantity of potassium sulphate.

(*c*) In order to expel all the water and to destroy the organic matter, the saline mass is calcined, and as this operation was formerly performed in cast-iron pots, the salt has obtained the name of potash. A calcining furnace, Fig. 278, is now used, distinguished from ordinary reverberatory furnaces by being provided with a double fire-place. These hearths, one of which is exhibited in section at *A*, Fig. 278, are placed at right angles

to each other, and the flame and smoke meeting in the centre of the furnace, pass off at *O*, the work-hole, into the chimney. Wood is used as fuel, and as the heating of the furnaces requires a very large quantity, they are only in use when a sufficient supply of crude potash is ready for operating on. The furnace is thoroughly heated in about five to six hours, care being taken to fire gradually, and to bring the interior of the furnace to nearly red heat, so that the vapour due to the combustion of the wood may not condense inside the furnace, but be carried off by the flue. The crude potash, broken up to egg-sized lumps, is next added in such quantities at a time as may suit the size of the calcining hearth; for instance, if the hearth is fitted to contain 3 cwts., that quantity is divided into three portions and put in at intervals of a few minutes. The first effect of the heat is to expel the water from the potash, the escape of the steam being promoted by stirring the mass with iron rakes. In about an hour all the water is driven off, and the mass takes fire in consequence of the burning of the organic matter, the salt at first being blackened, but gradually becoming white as the carbon burns off. As soon as this stage is reached, the potash is removed to the cooling-hearth, and, when cold, packed in well-made wooden casks, which, as this salt is very hygroscopic, are rendered as air-tight as possible. The heat of the furnace has to be well regulated to prevent the potash becoming semi-fused, in which case it would attack the siliceous matter of the fire-bricks; the workmen from time to time take a small sample to test how far the calcination is complete.

Fig. 278.



We, in Europe, obtain a considerable quantity of potash from the United States and Canada, known as American potash, of which there are three kinds, viz.:—1. Potash prepared as described. 2. Pearl-ash, or potash, purified by lixiviation, decantation from sediment, boiling down, and the calcination of the salt thus obtained. 3. Stone-ash, a mixture of uncalcined potash (potassium carbonate) and caustic potash, obtained by treating the crude potash liquor with caustic lime, and boiling down the mass to dryness; this article has the appearance of the crude caustic soda of this country, but is usually coloured red by oxide of iron; the lumps, stone-hard, are from 6 to 10 centimetres in thickness, and contain upwards of 50 per cent. caustic potash. The under-mentioned analyses exhibit the varying composition of the potash of commerce:—Sample 1 is from Kasan (Russia); analyst, M. Herman. 2. Tuscany. 3 and 4—the latter of a reddish colour—from North America. 5. Russia. 6. Vosges (France); analyst of 2, 3, 4, 5, and 6, M. Pesier. 7. Helmstedt, in Brunswick; analyst, M. Limpritsch. 8. Russia; analyst, M. Bastelaer.

	1.	2.	3.	4.	5.	6.	7.	8.
Potassium carbonate	78·0	74·1	71·4	68·0	69·9	38·6	49·0	50·84
Sodium „	—	3·0	2·3	5·8	3·1	4·2	—	12·14
Potassium sulphate	17·0	13·5	14·4	15·3	14·1	38·8	40·5	17·44
„ chloride	3·0	0·9	3·6	8·1	2·1	9·1	10·0	5·80
Water	—	7·2	4·5	—	8·8	5·3	—	10·18
Insoluble residue	0·2	0·1	2·7	2·3	2·3	3·8	—	3·60

The calcined potash varies in colour, being either white, pearl-grey, or tinged with

yellow, red, or blue. The red colour is due to oxide of iron, the blue to the manganates of potash. It is a hard, light, porous, non-crystalline mass, never entirely soluble in water. Formerly, a large quantity of potash was obtained from the residues of wine-making and called vinasse, the semi-liquid left after the alcohol has been distilled from the wine, and containing, among other substances, argol, or crude potassium bitartrate; it was boiled down, and next calcined, yielding a kilo. of very good potash for every hectolitre of vinasse. The large quantity of potash thus formerly produced may be judged from the fact that nineteen of the wine-producing departments of France, those only where large quantities of wine are converted into alcohol, technically termed *trois-six* and *cinq-huit*, yield annually about 9 to 10 million hectolitres of vinasse, at the present time employed for the preparation on a large scale of cream of tartar, glycerine, and tartaric acid.

5. *Salts of Potassium from the Treacle or Molasses of Beet-root Sugar.*—Of late years, the manufacture of potash salts from the vinasse left after the distillation of fermented beet-root molasses has been added as a new branch of industry by M. Dubrunfaut, and introduced into Germany by M. Varnhagen, in the year 1840, at Mucrena, Prussian Saxony.

Beet-root, on being subjected to ignition, yields an ash containing a large percentage of potash, a fact first observed in the early part of this century by M. Mathieu de Dombasle, a celebrated French agriculturist, who discovered that 100 kilos. of dried beet-root leaves yield 10·5 kilos. of ash, containing 5·1 kilos. of potash; but this author's idea that the leaves might be cut off and gathered for the purpose of potash manufacture proved erroneous, in so far that the growth of the roots was greatly impeded. After the publication of M. Dubrunfaut's researches on this subject, in 1838, the vinasse of the beet-root molasses distillation was evaporated to dryness, next calcined, and the calcined mass refined for the production of potash and other salts of that base, an industry which has obtained a great development, as may be judged from the fact that the quantity of these materials produced on the European continent in 1865 amounted to 240,000 cwts.

The reader who desires details on this subject is referred to the work, *On the Manufacture of Beet-Root Sugar in England and Ireland*, by Wm. Crookes, F.R.S., &c., p. 250 *et seq.*

The molasses from beet-root sugar consists, previous to fermentation and distillation, of the under-mentioned substances, as recorded by the several analysts whose names are subjoined:—

	Brunner.	Fricke.	Lunge.	Heidenpriern.	
Water	15·2	18·0	18·5	19·0	19·7
Sugar	49·0	48·0	50·7	46·9	49·8
Salts and organic substances .	35·8	34·0	30·8	34·1	30·5

The following analyses by M. Heidenpriern exhibit the average composition of the ashes of molasses:—

	1.	2.	3.
Potassa . . .	51·72	47·67	50·38
Soda	8·00	11·43	8·29
Lime	5·04	3·60	3·12
Magnesia . . .	0·18	0·10	0·18
Carbonic acid . .	28·90	27·94	28·70

The remainder of the 100 parts consists of phosphoric and silicic acids, chlorine, oxide of iron, &c. The quantity of such substances amounts to 10 or 12 per cent. According to Dubrunfaut, the alkalimetrical degree of the ash of beet-root sugar molasses is a constant, as the ash obtained from 100 grammes of molasses neutralises on an average 7 grammes of sulphuric acid (H_2SO_4).

The molasses is generally treated in the following manner :—It is first diluted with either water or vinasse to 8° or 11° B. = 1·056 or 1·078 sp. gr., and mixed with 0·5 to 1·5 per cent. of a pure mineral acid, the object of this addition being not simply the neutralisation of the alkali, but also the conversion of dextrine and such unfermentable sugar into fermentable sugar. Formerly, sulphuric acid was used, but upon the recommendation of M. Wurtz, hydrochloric acid is now generally employed, the advantage being the formation of readily soluble chlorides, instead of comparatively insoluble alkaline sulphides, by the action of the organic matter present in the molasses.

The diluted molasses is next mixed with yeast, left to ferment, and the alcohol distilled off; the residue is a liquid of about 4° B. density [= 1·027 sp. gr.] containing undecomposed yeast, ammoniacal salts, various organic substances, and all the inorganic salts of the beet-root juice. The potassa is present in this liquid as nitrate chiefly, although by the addition of hydrochloric acid a portion of this salt is decomposed, red nitrous fumes sometimes being seen in the fermentation room. Evrard suggested that the saltpetre should be separated from the beet-root molasses by evaporation, and further purified by the aid of the centrifugal machine. The acidity of the vinasse is neutralised by chalk, and afterwards it is evaporated to dryness in an iron vessel, the total length of which is 20·3 metres, by an average width of 1·6 metre, extended at the top to 2 metres, the depth being 0·34 metre. The vessel is made of stout boiler plate, strengthened by stays and angle irons, and is divided into two divisions, the larger of which has a length of 14·2 metres, and is the real evaporating pan, while the other is used as a calcining furnace, and covered with an arch of fire-bricks 0·6 metre high. The fire-place is 1·3 metre wide, and the fire-box has a surface of 3·3 square metres. The evaporation is effected by surface heating, that is to say, the flame and hot gases from the burning fuel after passing across the fire-bridge are conducted over the surface of the vinasse, the calcining pan being nearest to the fire, while the evaporating pan is at its other extremity in contact with the flue or chimney. The vinasse, having been run off from the still, is kept in cisterns, from which it is forced by means of a pump into a reservoir so placed as to admit of the liquid running in a constant stream into the evaporating pan. At a first operation both the evaporating and the calcining pan are filled with vinasse, but afterwards the latter is filled regularly with concentrated thick liquor, which is simply carbonised, only the organic matter being destroyed.

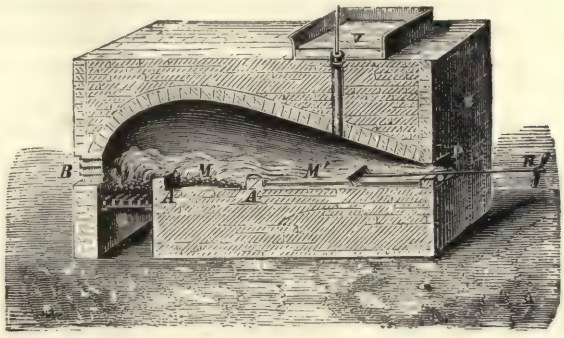
The daily average of carbonised vinasse is about 5 to 5½ cwts. The composition of that substance may be gleaned from the following approximative analysis :—

Insoluble matter	= 23·00	per cent.
Potassium sulphate	= 11·07	„
„ chloride	= 11·61	„
„ carbonate	= 31·40	„
Sodium „	= 23·26	„
Silica and potassium thiosulphate . .	= traces	„
	100·34	„

In Germany the calcined vinasse is generally sold to saltpetre manufacturers, but in Belgium and France this material is calcined, lixiviated, and the salts it contains separately obtained. For this purpose the vinasse is first evaporated to 38° or 40° B. (1·33 to 1·35 sp. gr.), and next carbonised and calcined in a furnace constructed as exhibited in Fig. 279. *V* is a reservoir containing the concentrated vinasse, which by means of a tube is gradually run into a furnace, of which *G* is the fire-place, *M* the calcination space, destined to contain the concentrated or carbonised vinasse, which is evaporated to dryness and calcined in *M'*; a door is fitted to each compartment, and at *P*, the end of the furnace opposite to the fire-place. The air required for the calcina-

tion is admitted partly through the ash-pit, partly through the openings, *B*, in the brickwork. The thickish liquid vinasse admitted into *M'* is constantly stirred, and, as soon as it is quite dry, it is shovelled across the brickwork bridge, *A'*, into the calcining space, *M*, care being taken to again fill *M'* with concentrated vinasse. The organic matter of the saline mass soon takes fire, emitting noxious fumes. The calcination is greatly aided by the access of air at *B*, and also to some extent by the potassium nitrate present. The temperature has to be regulated to prevent the salts becoming fused and forming a hard compact mass, in which case the potassium sulphate would be reduced to potassium sulphide, a salt which could not be removed. The calcined vinasse, technically termed *salin*, contains, when removed from the surface, 10 to 25 per cent. of insoluble substances, viz., calcium carbonate and phosphate, more or less charcoal, and, in addition, 3 to 4 per cent. moisture; the remainder consists of potassium and sodium carbonates, potassium sulphate and chloride, and sometimes cyanide in considerable quantity. The relative quantities of potassa and soda are, of course, not at all constant, but vary according to the soil on which the beets have grown; it has been observed in France that the molasses obtained from beets grown in the Department Nord are less rich in potassa than those grown in the Departments Oise and Somme. The average composition of the saline is—

Fig. 279.



7 to 12	per cent.	of potassium sulphate.
18 to 20	„	of sodium carbonate.
17 to 22	„	of potassium chloride.
30 to 35	„	of „ carbonate.

The complete composition of the saline may be gathered from the following tabulated results:—

	a.	*b.*	*c.*	*d.*
Water and insoluble matter . .	22·20	19·82	17·47	13·36
Potassium sulphate . . .	12·95	9·88	2·55	3·22
„ chloride . . .	15·80	20·59	18·45	16·62
Rubidium „ . . .	0·13	0·15	0·18	0·21
Sodium carbonate . . .	25·52	19·66	19·22	16·54
Potassium „ . . .	23·40	29.90	42·13	50·05
	100·00	100·00	100·00	100·00

The method of separating the soluble salts from each other invented by M. Kuhlmann is generally executed as follows:—The saline mass is first broken up and granulated by the aid of grooved iron rollers, after which it is placed in lixiviation-tanks, each containing 26·4 cwts., and arranged precisely in the same manner as those in use in soda works. The liquor tapped from the tanks has a sp. gr. of 1·229 (= 27° B.); the insoluble residue is used as manure. The liquor having been collected in a large reservoir, capable of containing some 210 hectolitres, is concentrated by waste heat (*abgängige wärme*) to a density of 1·26 (= 30° B.); on cooling, the greater part of the potassium sulphate crystallises, and is removed, care being taken to wash off the adhering mother-liquor. The sulphate thus obtained contains 80 per cent. pure

potassium sulphate, the rest being carbonate of potassa and organic matter; this material is converted into potash by Leblanc's process. The liquor at 30° B. is next poured into evaporating-pans, each capable of containing 90 hectolitres, and concentrated by means of heat and a steam pressure of 3 atmospheres (= 45 lbs. to the square inch) to a density of 42° B. (= 1·408). By this operation a mixture of sodium carbonate and potassium sulphate is separated, which frequently exhibits 30 alkalimetrical degrees; the liquor is transferred from the evaporating-pans to crystallising vessels, in which it is cooled down to not less than 30°. If, by carelessness, the temperature should fall below 30°, the potassium chloride crystals become mixed with a layer of sodium carbonate. The liquor at a temperature of 30°, and having a density of 42° B., is again transferred to evaporating-pans each capable of containing 20 hectolitres, and evaporated in winter to a sp. gr. of 1·494 (= 48° B.), and in summer to a sp. gr. of 1·51 (= 49° B.). By this operation sodium carbonate separates, the first and purer proportions of which are of 82 alkalimetrical degrees, and the last of 50° only. After the separation of the salt, the remaining liquor is poured into small crystallising vessels, each capable of holding $2\frac{1}{2}$ hectolitres, and, having been left standing for some time, yields in each vessel about 130 kilos. of a crystalline salt, mainly composed according to the formula $K_2CO_3 + Na_2CO_3 + 12H_2O$. The remaining mother-liquor, when evaporated to dryness and calcined, yields a semi-refined potash, tinged with red by oxide of iron. This product is again lixiviated with water, and the liquor, having been concentrated to 1·51 to 1·525 sp. gr. (= 49° to 50° B.), deposits a large quantity of potassium sulphate and sodium carbonate. The mother-liquor, having been again evaporated and calcined, yields a potash consisting of 100 parts of—

Potassium carbonate	91·5
Sodium „	5·5
Potassium chloride and sulphate . . .	3·0
	100·0

The sodium carbonate possessing a strength of 80 to 85 alkalimetrical degrees is refined by being washed with a very concentrated aqueous solution of sodium carbonate, and thus brought to a strength of fully 90 alkalimetrical degrees.

The sulphate of potassa, chloride of potassium, and the double salt of the two carbonates are purified and re-crystallised. The following analyses exhibit the composition of refined potash obtained from beet-root sugar molasses:—

	a.	*b.*	*c.*
Potassium carbonate . . .	88·73	94·39	89·3
Sodium „ . . .	6·44	traces	5·6
Potassium sulphate . . .	2·27	0·28	2·2
„ chloride . . .	1·00	2·40	1·5
„ iodide . . .	0·02	0·11	—
Water	1·39	1·76	—
Insoluble substances . .	0·12	—	—

a and *b* are from Waghäusel in Baden; *c* is doubly refined French potash. The crude potash from beet-root sugar-works, a product not to be confused with *salin*, is composed as follows:—

	a.	*b.*	*c.*	*d.*	*e.*
Potassium carbonate .	53·9	79·0	76·00	43·0	32·9
Sodium „ . .	23·1	14·3	16·30	17·0	18·5
Potassium sulphate . .	2·9	3·9	1·19	4·7	14·0
„ chloride . .	19·6	5·8	4·16	18·0	16·0

a is a French product; *b*, from Valenciennes; *c*, from Paris; *d*, Belgian; *e*, from Magdeburg, Prussia.

With recent improvements in the manufacture of beet-sugar the production of the treacle, which is not fit for human consumption, has been much reduced. Consequently, less potash is obtained from this source.

6. *Salts of Potassium from Sea-weeds.*—Potassa salts are obtained in large quantities from various sea-weeds, as a bye-product of the manufacture of bromine and iodine. The three following methods are employed for this purpose :—

(*a*) The old calcination method, consisting in a complete reduction of the weeds to ash, and the methodical lixiviation of that product, so as to obtain various salts by crystallisation.

(*b*) The carbonisation on Stanford's method, consisting in the dry distillation of the weeds to convert them into a carbonaceous mass, afterwards lixiviated, while products are simultaneously obtained the sale of which considerably lessens the cost of the preparation of the potassa salts.

(*c*) A third mode of treatment, that of Kemp and Wallace, consisting in boiling the weeds with water, evaporating the solution, and carefully incinerating the residue.

The oldest method is still the most generally employed in France, on the coasts of Brittany and Lower Normandy, especially in the neighbourhood of Brest and Cherbourg, and in Scotland and Ireland.

The process is mainly conducted as follows :—After drying in the air, the plants are incinerated, the result of which is the formation of a black semi-fused mass, which in France is termed *Varech* or *Vraic*, and in England and Scotland is known as *kelp*. A distinction is made between the kelp obtained by the incineration of the weeds, *Fucus serratus* and *Fucus nodosus*, found on rocks near the sea-coast, and the kelp obtained from the plant botanically known as *Laminaria digitata*, thrown up on the coast during the storms. The latter is richer in potassa salts, but contains much less iodine; it is found plentifully on the western coasts of Scotland and Ireland, while on the eastern coast of the British Isles the other weed is the chief source of kelp, having an average composition of—

Insoluble matters	57·000
Sodium sulphate	10·203
Potassium chloride	13·476
Sodium ,, ...	16·018
Iodine	0·600
Other salts	2·703
	100·000

The best kelp met with in commerce is that from the island of Rathlin, the value at Glasgow amounting to £7 10*s.* to £10 10*s.* per ton of 22½ cwts.; while Galway kelp is valued at only £2 or £3 per ton, owing to the large quantity of salt it contains. Twenty-two tons of moist sea-weed yield—

Medium kelp	1 ton
Potassium chloride	5 to 6 cwts.
,, sulphate	3 cwts.

The Scotch mode of treating kelp is briefly the following :—The material is first broken into small lumps, and put in large iron cauldrons, hot water being added to exhaust all the soluble matter. This operation follows the method of the manufacture of soda from common salt, to be presently considered. The water is first made to act upon nearly exhausted kelp, and at last with quite fresh kelp, until a liquid is produced marking 36° to 40° Tw. = 1·18 to 1·20 sp. gr. The insoluble residue contains chiefly silica, sand, calcium and magnesium carbonates, their sulphates and phosphates,

and particles of charcoal, and is used for bottle-glass manufacture. The liquor from the kelp is evaporated in large cast-iron semi-globular cauldrons by the direct action of a coal fire, and contains chiefly potassium chloride, a comparatively small quantity of sodium chloride, potassium sulphate and chloride, some sodium carbonate, potassium iodide and sulphide, and potassium and sodium dithionites. The mode of separating these salts from each other is based upon their varying solubility in water, and is therefore conducted by alternate evaporation and cooling. As the potassium sulphate is the least soluble, it falls to the bottom of the cauldron during the first evaporation, and is collected by the workmen by means of perforated ladles, and brought into the trade as *plate sulphate*. After this salt has been collected the liquid is run into coolers, in which the greater bulk of the potassium chloride crystallises; the mother-liquor from these crystals is again transferred to the evaporator, and by the continued application of heat, and consequent concentration, the common salt is separated. It should be borne in mind that common salt is scarcely more soluble in hot than in cold water, while the solubility of most other salts is greatly increased by a higher temperature; it is therefore possible to push the evaporation and concentration to the point of incipient precipitation of the potassium chloride, the common salt being then ladled out of the cauldron, and the liquid again run into the coolers in order to obtain another deposit of potassium chloride, always more or less contaminated with common salt. This operation is repeated four times; the first crop of potassium chloride contains from 86 to 90 per cent. of this salt, the remainder is chiefly potassium sulphate; the second and third crop yield a very pure salt, 96 to 98 per cent. of potassium chloride; the fourth crop contains some sodium sulphate mixed with the potassium chloride. The liquor left after the fourth crystallisation having a sp. gr. = 1·33 to 1·38 = 66° to 76° Tw., and containing among other compounds sodium sulphate, alkaline sulphides, thiosulphates and carbonates, and iodide of potassium, is not submitted to further evaporation, but, having been poured into shallow vessels placed in the open air, is mixed with dilute sulphuric acid, sulphuretted hydrogen and carbonic acid gases being largely evolved, while, in consequence of the decomposition of the polysulphides and thiosulphates, a thick foam of pure sulphur appears on the surface of the liquid. The sulphur is ladled off, and after having been washed on filters and dried, is sold. Almost as soon as the evolution of gas ceases, there is added to the liquid more sulphuric acid and some manganese, and the mixture treated for the preparation of iodine (*quod vide*).

In order to guard against loss of valuable substances by volatilisation during the crude and imperfect mode of incineration, it has been tried to simply carbonise the weeds (Stanford's method). The weeds are first dried and strongly pressed into the shape of peat blocks; these are submitted to dry distillation in retorts arranged similarly to those in gas-works. The products of the dry distillation collected in the usual manner contain in 100 parts of fresh weed—

68·5	to 72·5	parts	of ammoniacal liquor
4·0		„	tar
7·0	to 7·5	„	carbonised weed or coke-weed
2·0	to 2·5	„	illuminating gas

The coke contains 33 per cent. carbon, the remainder consisting of alkaline and earthy salts; the volatile products of the distillation are treated for paraffine, photogen, acetic acid, and ammoniacal salts, the gas being used for lighting purposes. Although Mr. Stanford's mode of treatment is undoubtedly rational, there are difficulties in its practical execution which have prevented its adoption in Scotland as well as in France. The quantity of potash salts obtained from sea-weeds in the year 1865 amounted,

according to M. Joulain, to a total of 2,700,000 kilos., of which the United Kingdom produced 1,200,000 kilos., the remainder being furnished by France.

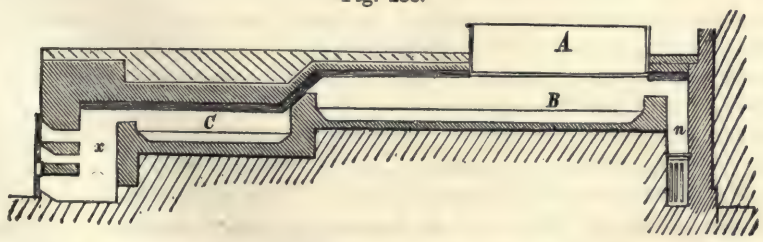
Since the production of potassium chloride at Stassfurt and Kalucz has become so extensive, that of potassa salts from sea-weeds is of little consequence.

7. *Salts of Potassium from the Suint of Wool.*—Raw wool contains about 20 per cent. of suint soluble in cold water. It consists of the potassium compounds of oleic, stearic, and acetic acids with a little valerianic acid and many other organic matters, as well as potassium chloride and sulphate, ammonium compounds, and generally potassium carbonate or some sodium compounds. The portion of raw wool soluble in carbon disulphide consists essentially of cholestearine, and a smaller proportion of iso-cholestearine, partly free, but chiefly combined with fatty acids and a little benzoic acid. The recent researches of Chludinsky show how these substances differ in their proportions. He has determined both the moisture and the quantity of matter soluble in water and in carbon disulphide in average samples of the fleeces of different herds of sheep.

Race and Characters of Sample.	Moisture.	Loss in Water.	Loss in Carbon Disulphide.	Pure Wool.
Merino { Negretti ram, from Konska-Wola	15·42	47·28	21·61	15·69
Merino { „ „ „ „	11·72	54·73	13·33	20·22
Merino { Negretti sheep „ „	11·81	44·54	26·10	17·55
Merino { Australian ram	13·23	33·57	13·24	39·96
Merino { Rambouillet ram, from Karlow	11·45	46·95	14·83	26·77
Southdown, from Poland	8·18	62·41	4·61	24·30
Do. from England	11·90	39·21	9·73	39·16
Oxfordshire sheep, from Poland	10·85	41·27	4·83	43·04
Holstein „ „ „	8·04	51·02	8·25	32·69
„ „ „ „	15·83	25·14	0·95	58·08
Wool from Buenos-Ayres	11·87	16·10	4·91	67·12
Black wool, from Podolia	12·23	5·66	1·82	80·29
„ „ „ Kijew Government	11·59	3·61	0·88	83·92
„ „ „ Wolhynia Government	10·60	6·35	2·45	80·60
White wool, from Radom Government	10·70	7·40	0·65	81·21

Maumené and Rogelet took out an English patent for obtaining potash from wool, and showed the first specimens of this new product at the London Exhibition of 1862. The raw wool compressed in casks was extracted with cold water, the liquid obtained, of the sp. gr. 1·01, was concentrated, the brown residue, "potassium suintate," was ignited in retorts to yield lighting-gas, and the residual carbonaceous matter yielded a pure potash on lixiviation. The treatment of suint was introduced into Germany by

Fig. 280.



F. Hartmann, and there are now works for this purpose at Doehren, Bremen, &c. In France there are many such establishments—at Roubaix, Rheims, Elbœuf, &c.; and at Liége, Verviers, and Antwerp in Belgium. The evaporation of the lyes is conducted in Germany and Belgium in reverberatories. At Doehren, the liquors from the ext tion of the wool are pumped into an iron tank *A* (Fig. 280), where they undergo

a preliminary heating from the combustion of the escaping gases, and are then pumped into the evaporator, *B*. The condensed residues are next removed into the calcining space, *C*. As soon as they have been thoroughly dried by the flames coming from the fire-box, *x*, the fatty matter, dirt, &c., burn, giving off considerable heat, so that, by regulating the access of air, it is possible to evaporate 12 kilos. of liquid, with 1 kilo. of coal. The fire-box, the calcining space, and the evaporator are built of fire-proof tiles or stones, and the chimney, *n*, is constructed of fire-bricks. The crude potash contained—

Soluble salts	92·05 per cent.
Insoluble salts	4·92 „
Organic matter	3·03 „

The soluble salts had the following composition—

Potassium carbonate	85·34 per cent.
„ chloride	6·15 „
„ sulphate	2·98 „
Sodium carbonate	5·02 „

A part of the impurities is derived from the river water used for lixiviation. W. Graff, of Lesum, in 1878, worked up the crude potash from six wool washeries to pure potassium carbonate, bicarbonate, chloride, and sulphate.

Wérotte, of Verviers, found, in 1873, in two samples of potash from suint—

Potassium carbonate	68·50 per cent.	...	64·30 per cent.	
„ sulphate	2·10 „	...	2·49 „	
„ silicate	8·50 „	...	8·00 „	
„ chloride	12·50 „	...	16·88 „	
Sodium carbonate	3·20 „	...	3·10 „	
Water	2·77 „	...	2·80 „	
Insoluble	1·48 „	...	1·55 „	
Loss	0·95 „	...	0·88 „	

Altogether about 1000 tons of potash are obtained from suint every year.

Pure potassium carbonate as it is met with in laboratories was formerly obtained by igniting tartar, or a mixture of tartar and saltpetre, or by calcining potassium acetate. At present it is produced by the cautious ignition of a mixture of potash saltpetre with an excess of charcoal, by igniting potassium bicarbonate, or by precipitating a solution of potassium chloride with ammonium dicarbonate in presence of alcohol. In England potassium carbonate is made industrially for the manufacture of flint-glass, which owes its freedom from colour not merely to the use of lead-glass, but also to the employment of quite pure materials. The pure crystalline potassium carbonate, containing 16 to 18 per cent. of moisture (corresponding approximately to the formula, $4K_2CO_3.7H_2O$), is met with in the form of small cubes. The raw material is the American pearl-ash, which is melted in a furnace of the construction of a common side-furnace, with the addition of sawdust in order to convert the potassium hydroxide and sulphide into carbonate. The melted ash is dissolved, the solution let settle, drawn off clear from the sediment, and evaporated down in a reverberatory, when the mass appears as a blackish-grey powder. It is again dissolved, the solution clarified by standing, and evaporated to dryness in a third reverberatory, when the product is white. It is now dissolved for the third time, evaporated until all the potassium sulphate has crystallised out, and the mother-liquor is again evaporated until on cooling it forms a crystalline mass with the above-named proportion of water.

Table of the Proportion of Potash in Lyes according to Specific Gravity at 15°.

Specific Gravity.	Baumé.	Twaddell.	Per cent. K_2CO_3.	1 cubic metre contains kilos. of K_2CO_3.	Specific Gravity.	Baumé.	Twaddell.	Per cent. K_2CO_3.	1 cubic metre contains kilos. of K_2CO_3.
1·014	2°	2·8°	1·5	15	1·241	28°	48·2°	24·5	304
1·029	4	5·8	3·1	32	1·263	30	52·6	26·6	336
1·045	6	9·0	4·9	51	1·285	32	57·0	28·5	366
1·060	8	12·0	6·5	69	1·308	34	61·6	30·7	402
1·075	10	15·0	8·1	87	1·332	36	66·4	32·7	436
1·091	12	19·2	9·8	107	1·357	38	71·4	34·8	472
1·108	14	21·6	11·6	129	1·383	40	76·6	37·0	512
1·125	16	25·0	13·3	150	1·410	42	82·0	39·3	554
1·142	18	28·4	15·0	171	1·438	44	87·6	41·7	600
1·162	20	32·4	17·0	198	1·468	46	93·6	44·0	646
1·180	22	36·0	18·8	222	1·498	48	99·6	46·5	697
1·200	24	40·0	20·7	248	1·530	50	106·0	48·9	748
1·220	26	44·0	22·5	275	1·563	52	112·0	51·3	802

Caustic potash (potassium hydrate, KOH) is at present obtained on the large scale. The chief method consists in lixiviating potassium carbonate (as obtained from potassium chloride by the Leblanc process) in the state of crude potash (*i.e.*, mixed with calcium sulphate and hydrate as it comes from the calcining furnace) with water and causticising by treatment with lime. It is more advantageous—*i.e.*, an economy of time and materials—if the coal added to the mixture of potassium sulphate and limestone is used in a larger proportion, if the smelting is protracted, and if the crude potash obtained is at once lixiviated with water at 50°. Thereby the subsequent causticising with lime is avoided. The lye is evaporated to dryness in pans, scooping out the foreign salts as they separate.

Table of the Specific Gravity of Potash Lye at 15°.

Specific Grevity.	Baumé.	Twaddell.	100 parts contain KOH.	1 cubic metre contains kilos. KOH.	Specific Gravity.	Baumé.	Twaddell.	100 parts contain KOH.	1 cubic metre contains kilos. KOH
1·014	2°	2·8°	1·7	17	1·220	26°	44·0°	24·2	295
1·029	4	5·8	3·5	36	1·241	28	48·2	26·1	324
1·045	6	9·0	5·6	58	1·263	30	52·6	28·0	353
1·060	8	12·0	7·4	78	1·285	32	57·0	29·8	385
1·075	10	15·0	9·2	99	1·308	34	61·6	31·8	416
1·091	12	18·2	10·9	119	1·332	36	66·4	33·7	449
1·108	14	21·6	12·9	143	1·357	38	71·4	35·9	487
1·125	16	25·0	14·8	167	1·383	40	76·6	37·8	522
1·142	18	28·4	16·5	188	1·410	42	82·0	39·9	563
1·162	20	32·4	28·6	216	1·438	44	87·6	42·1	605
1·180	22	36·0	20·5	242	1.468	46	93·6	44·6	655
1.200	24	40·0	22·4	269	1·498	48	99·6	47·1	706

Statistics.— The yearly production of potash according to H. Grüneberg is—

Wood-ashes.—Russia, Canada, U.S. of North America, Hungary, and Galicia	20,000 tons
Beet-sugar ash.—France, Belgium, Germany	12,000 „
Mineral potash.—Germany, France, England	15,000 „
Suint.—Germany, France, Belgium, Austria	1,000 „
	48,000 „

These conditions differ strikingly from those which existed thirty years ago, when wood-ash was in exclusive use and Russian potash ruled the market. The potash extracted from wood-ashes scarcely amounts to one-half of the total production; it decreases year by year, and the time when it will disappear from the market seems within measurable distance. It is being superseded by beet potash, which is a bye-product of the beet-sugar manufacture, and hence can be offered at lower prices. Of

greater importance is the manufacture of potash from potassium sulphate, based on the resources of the Stassfurt salt-beds. The centre of production of beet potash is in the north of France, that of mineral potash in Northern Germany, which is now the greatest potash-producing country in the world.*

Alkalimetry.—Commercial potash is commonly a mixture of caustic potash with potassium carbonate and other potassium and sodium salts (as soda itself is a mixture of sodium carbonate with foreign salts, especially sulphate and chloride). In order easily and quickly to ascertain the proportion of pure potassium carbonate in a sample of potash with an accuracy sufficient for technical purposes there are two methods, namely—

(*a*) To determine the quantity of acid required to neutralise the potassium carbonate;

(*b*) To find the quantity of carbonic acid which can be expelled from potash by the addition of a stronger acid.

Both methods, of course, are applicable only if besides the alkaline carbonate no other carbonates are present in the potash. All procedures for determining the potassium carbonate in a sample of potash are called potassimetric methods. The methods of testing potash and soda (sodametric) are included under the common name alkalimetric.

As a normal solution Mohr uses crystalline oxalic acid ($C_2H_2O_4.2H_2O = 126$); 63 grammes oxalic acid ($= \frac{1}{2}$ mol.) are dissolved in water and made up exactly to $\frac{1}{2}$ litre. To this acid solution there corresponds a second, a solution of caustic potassa (KOH). It is so adjusted that on mixture with an equal volume of the oxalic acid solution the last drop of the potassium solution turns the colour of the litmus solution added from red to blue which can always be effected by a single drop if the solution is free from carbonic acid. For testing alkali $\frac{1}{20}$ mol. in grammes of the anhydrous ignited sample is weighed off, containing, therefore, 6·911 grammes potash or 5·32 soda. As the standard acid contains in 1000 c.c. $\frac{1}{2}$ mol. oxalic acid, 100 c.c. of this liquid will saturate exactly $\frac{1}{20}$ mol. of the alkali. The potash along with a solution of litmus is placed in a small boiling flask and a little of the acid is run in, which decomposes the potash with effervescence. The colour passes from blue to violet and the effervescence becomes slighter. The liquid is raised to a boil and more acid is dropped in until the colour becomes a full onion-red. Test acid is then run in excess. The alkali is now super-saturated, and the carbonic acid is expelled by boiling. The point of saturation of the alkali is now overstepped 5 or 6 c.c. A pipette graduated in $\frac{1}{10}$ c.c. is filled up to 0 with the standard caustic potash, and it is allowed to fall drop by drop into the liquid solution of the sample under examination, keeping it agitated. The colour passes from red to violet and then suddenly into a clear blue. The number of c.c. of the alkaline solution consumed is read off, and deducted from the c.c. of test acid consumed; the remainder shows pure potassium carbonate 3·45 grammes = $\frac{1}{40}$ mol. potash used, *e.g.*, 36 c.c. of test acid and 3 c.c. of test alkali = 33 c.c. of test acid = 66 per cent. of potassium carbonate (as instead of $\frac{1}{20}$ mol. only $\frac{1}{40}$ mol. was used, whence the c.c. of the acid must be doubled to obtain per cents.). Latterly, instead of litmus, cyanine, fluoresceine, phenolphthaleine, tropaeoleine 000, and phenacetaline have been proposed for alkalimetric and acidimetric indicators.

Fresenius and Will decompose potash with sulphuric acid and determine the amount of carbonic acid by the loss of weight.

Commercial Value.—As potash is very hygroscopic, in order to determine its commercial value it is by no means sufficient to state how much potassium carbonate is

* It must not be forgotten that beet potash can be continually obtained only by either gradually exhausting the soil of a necessary constituent of plant-food, or by continually using potash manure. Hence the beet-potash industry could not exist alone.

present; this statement must be referred to anhydrous potash, and we must know how much water is present. In order to ascertain the quantity of water, a weighed quantity of the sample, *e.g.*, 10 grammes, is heated until all water is expelled, for which five minutes are generally sufficient. The loss of weight expressed in decigrammes shows the amount of water per cent. Of the potash thus dried, 6·23 grammes are weighed out and treated as above. As 6·29 grammes potash and 4·84 grammes soda, if they were pure carbonates, would exactly contain 2 grammes carbonic acid, every 2 centigrammes of loss signify 1 per cent. of carbonate. If the loss of weight of the apparatus on testing a potash was 1·64 (= 164 centigrammes) the potash would contain $\frac{164}{2}$ = 82 per cent. of potassium carbonate.

According to H. Will and R. Fresenius, the statement of the percentage of potash should refer to the anhydrous condition. This percentage is expressed by the constant numerator of a fraction, whilst the varying proportion of water is shown by a varying denominator. If, *e.g.*, we wish to express that a potash in its anhydrous condition contains 60 per cent. potassium carbonate, we should write $\frac{60}{100}$; if the sample absorbed so much moisture that 100 kilos. increased in weight to 105 or 109, we should write $\frac{60}{105}$ or $\frac{60}{109}$. According to this system, the price of the product would be fixed by the manufacturer in its anhydrous state, and the contents of the article would be designated by a fraction in such a manner that the numerator shows the proportion of potassium carbonate, whilst the denominator 100 shows the absence of water. For instance, potash at $\frac{60}{100}$ is worth, say, 30*s*. The denominator augmented by the increase of water informs the buyer then how much of the hydrated article should be supplied for the same price. Thus 106 or 109 kilos. of the damp potash ought to be supplied at 30*s*.

The proportion of soda is generally expressed in "degrees." The French degrees are per cents. of sodium carbonate, whilst the English degrees are sodium oxide (caustic soda, Na_2O). As sodium carbonate consists of 58·6 parts soda and 41·4 parts carbonic acid in 100 parts,

80° French = 46·9 English
86° „ = 50·5 „
96° „ = 52·8 „

G. Lunge (*Dingler's Journal*) points out that the degrees used in the English soda trade only exceptionally show the percentage "real soda," Na_2O, as the molecular weight of sodium carbonate is taken at 54 instead of 53. Chemically pure sodium carbonate is consequently made to show 59·26 Na_2O instead of 58·49 per cent. (*i.e.*, 0·77 per cent. too much). In Lancashire they go still further, and put for 53 Na_2O, 54 "real soda," *e.g.*, 51·6 per cent. instead of 50 per cent. Even with this the trade was not satisfied, for on checking the results of certain Liverpool commercial chemists the returns, especially for caustic soda, were often found 2° to 3° too high. A soda of 58°, "*Liverpool test*," corresponds, therefore, not, as it ought, to 99·16 per cent. Na_2CO_3, but to scarcely more than 96 per cent.

The processes for the determination of alkali given above have grave defects, as they overlook soda contained in samples of potash and treat summarily the quantities of potassium salts. For the technicist they differ considerably in value; the carbonate is worth more than the chloride and the latter less than the sulphate. A complete analysis is necessary for ascertaining the value of potassium salts.

COMMON SALT AND SALT WORKS.

Occurrence.—Common salt, or chloride of sodium, consists of—

Chlorine, Cl	35·5	...	60·41
Sodium, Na	23·0	...	39·59
	58·5	...	100·00

and is found on our globe in the solid state as rock-salt, as well as dissolved in sea-water in enormously large quantities. It occurs as rock-salt in extensive layers, alternating with strata of clay and gypsum, at an average depth of 100 metres. The following are a few of the localities where rock-salt is met with in the tertiary formation:—Wieliczka, Poland; the northern slopes of the Carpathian mountains, and in several districts of Hungary; in the chalk formation of Cardona, Spain; in the Eastern Alps, Bavaria, Salzburg, Styria, and the Tyrol. Among the trias formation are the salt deposits of the Teutoburg-wood, Germany, and a great many others, among them the celebrated Stassfurt deposits. In England, rock-salt is found in Cheshire, this county being also plentifully supplied with saline springs, the water of which yields on evaporation an abundance of salt. Petroleum wells are found with salt in many parts of Asiatic Russia, in Syria, Persia, and the slopes of the Himalayas. Salt occurs plentifully in several districts of Africa, America, and other parts of the world, and mixed with clay and marl, forming salt-clay. Salt occurs secondarily by having been dissolved, at a depth varying in Germany from 91 to 555 metres, by water, which carries it again to the surface, there forming salt springs and salt lakes, from which the salt is obtained by evaporation. Among the salt lakes may be noticed the lake near Eisleben, Germany; the Elton Lake near the Wolga, Russia; the Dead Sea; and the Salt Lake of Utah, United States.

There can be no doubt that the common salt met with in salt springs owes its origin to the solvent action of water upon rock-salt; and as rock-salt is largely met with in sedimentary geological formations, the prevalence of this formation in Germany has there given rise to a large number of salt springs. Common salt is also found in sea-water, and if obtained by its evaporation is often termed sea-salt; or if deposited, as is the case in the Polar regions, by intense cold on the surface of ice-fields, it is known as *rassol*. Common salt is largely obtained as a bye-product of some chemical operations, as in the conversion of sodium-nitrate into potassium-nitrate by the aid of potassium chloride.

Method of Preparing Common Salt from Sea Water.—The constituent salts of sea-water do not differ in any part of the world; even the difference in quantity is very small, and is generally due to local causes, as the dilution of the sea-water by river-water, melting icebergs, &c. The specific gravity of sea-water, at 17°, varies from 1·0269 to 1·0289, the specific gravity of the water of the Red Sea being as high as 1·0306. One hundred parts of sea-water contain—

	Pacific Ocean.		Atlantic Ocean.		German Ocean.		Red Sea.
Sodium chloride . . .	2·5877	...	2·7558	...	2·5513	...	3·030
„ bromide . .	0·0401	...	0·0326	...	0·0373	...	0·064
Potassium sulphate . .	0·1359	...	0·1715	...	0·1529	...	0·295
Calcium sulphate . .	0·1622	...	0·2046	...	0·1622	...	0·179
Magnesium sulphate . .	0·1104	...	0·0614	...	0·0706	...	0·274
„ chloride . .	0·4345	...	0·3260	...	0·4641	...	0·404
Potassium „ . .	—	...	—	...	—	...	0·288
	3·4708	...	3·5519	...	3·4384	...	4·534

The composition of the salt contained in the water of the several seas is shown by the following table:—

——	Caspian Sea.	Black Sea.	Baltic.*	English Channel. Average of 7 localities.	Mediterranean. Average of 3 localities.	Atlantic Ocean. Average of 3 localities.	Dead Sea. Average of 5 localities.
Average quantity of salt and water—							
Solid salt . . .	0·63	1·77	1·77	3·31	3·37	3·63	22·30
Water	99·37	98·23	98·23	96·69	96·63	96·37	77·70
The dissolved solid matter consists in 100 parts of—							
Sodium chloride . .	58·25	79·39	84·70	78·04	77·07	77·03	36·55
Potassium „ . .	1·27	1·07	—	2·09	2·48	3·89	4·57
Calcium „ . .	—	—	—	0·20	—	—	11·38
Magnesium „ . .	10·00	7·38	9·73	8·81	8·76	7·86	45·20
Sodium and magnesium bromides .	—	0·03	—	0·28	0·49	1·30	0·85
Calcium sulphate . .	7·78	0·60	0·13	3·82	2·76	4·63	0·45
Magnesium „ . .	19·68	8·32	4·96	6·58	8·34	5·29	—
Calcium and magnesium carbonates .	3·02	3·21	0·48	0·18	0·10	—	—
Nitrogenous and bituminous matter .	—	—	—	—	—	—	1·00

One cubic metre (35·3165 cubic feet) of sea-water contains consequently about 28 to 31 kilos. of sodium chloride and 5 to 6 kilos. of potassium chloride. Sodium chloride (common salt) is obtained from sea-water :—

a. By the evaporation of the water by the aid of the sun's heat.

b. In winter, by freezing.

c. By artifical evaporation.

Method of Obtaining Common Salt in Salines.—This method of obtaining common salt from sea-water is limited to certain of the coast-lines of Southern Europe, and is never effected beyond 48° N. latitude. The countries best situated for this industry are France, Portugal, Spain, and the coasts of the Mediterranean. The arrangement of the salines, or salt-gardens, is the following :—On a level sea-shore is constructed a large reservoir, which, by a short canal, communicates with the sea, care being taken to afford protection against the inroads of high tides. The depth of water in these reservoirs varies from 0·3 metre to 2 metres. The sea-water is kept in the reservoir until the suspended matter has been deposited, and is then conveyed by a wooden channel into smaller reservoirs, from which it is conducted by underground pipes to ditches surrounding the salines, where the salt is separated from the water. The salt is collected, placed in heaps on the narrow strips of land which separate the ditches from each other, and sheltered from rain by a covering of straw. As these heaps are left for some time, the deliquescent magnesium and calcium chlorides are absorbed in the soil; consequently, the salt is comparatively pure. The mother-liquor is used in the production of potassium chloride, sodium sulphate, and magnesium salts, the process employed being that originally suggested by Professor Balard, and afterwards improved by Merle.

By Freezing.—This process is based upon the fact that when a solution of common salt is cooled to several degrees below the freezing-point, it is split up into pure water, which freezes, and a strong brine. The solution becomes more concentrated by repeated freezing and removal of the ice, until at last a solution is obtained which by a slight evaporation yields a crop of salt. In order to render the product purer, some lime is added to the solution before evaporation to decompose the magnesia salts.

* According to the experiments of Baron Sass, the water of the Baltic from the Great Sound between the Islands of Oesel and Moon only contains 0·666 per cent. of solid matter, and is of a sp. gr. = 1·00474.

By Artificial Evaporation.—Common salt evaporated from sea-water by the aid of fuel, or *sel ignifère*, is chiefly prepared in Normandy, in the following manner:—The sand impregnated with salt is employed to saturate the sea-water, which is next evaporated. Very frequently an embankment of sand is thrown up on the shore, so as to be covered at high tides only; in the interval between two tides a portion of the salt dries with the sand, which in hot summer weather is collected twice or three times daily. The sand is lixiviated in wooden boxes, the bottoms of which are constructed of loose planks covered with layers of straw; the sand having been put in the boxes, sea-water is allowed to percolate through them till the specific gravity of the water increases to 1·14 or to 1·17, the density being observed by means of three wax balls weighted with lead. The salt boilers at Avranchin consider that a solution of brine of 1·16 sp. gr. is the most suitable for evaporation. The evaporation is carried on in leaden pans, and during the process the scum is removed and fresh brine added until the salt begins to crystallise out, when again a small quantity of brine is added to produce more scum, which is at once removed, and the evaporation continued to dryness. The salt thus obtained, a finely divided but very impure material, is put into a conical basket suspended over the evaporating pan, the object being to remove by the action of the steam the deliquescent calcium and magnesium chlorides. The salt is next transferred to a warehouse, the floor of which is constructed of dry, well-rammed, exhausted sand, and here it is gradually purified by the loss of deliquescent salts, the consequent decrease in weight amounting to 20 to 28 per cent. 700 to 800 litres of brine yield, according to the quantity of salt contained in the sand, 150 to 250 kilos. of salt. A very similar method is in use at Ulverstone, Lancashire.

At Lymington and in the Isle of Wight, sea-water is concentrated by spontaneous evaporation to one-sixth of its original bulk, the brine being then evaporated by the aid of artificial heat. In the neighbourhood of Liverpool, salt is obtained by employing sea-water in refining crude rock-salt; in this way at least 2·3 per cent. of common salt results as a bye-product. During a continuation of hot summer weather salt is deposited from the water of many of the salt lakes in immense quantities, amounting, for instance, at the Elton Lake, Russia, to twenty millions of kilos.

Rock-salt.—This mineral is frequently accompanied by anhydrite, clay, and marl, and is sometimes found in what are termed pockets of irregular shape, interspersed with clay. Again, in some cases saline deposits are separated by layers of marl. With rock-salt other minerals sometimes occur, as, for instance, brongniartine ($Na_2SO_4 + CaSO_4$), near Villarubia, in Spain, and the remarkable minerals of the salt deposit near Stassfurt. Above the latter deposit is a layer, 65 metres thick, of bitter, many-coloured, deliquescent salts, consisting of 55 per cent. of carnallite, sylvin, and kainite; 25 per cent. of common salt; 16 per cent. of kieserite; and 4 per cent. of magnesium chloride. As this saline layer contains 12 per cent. of potassa, it is an important deposit in an industrial sense.

The composition of rock-salt is as follows:—

I. White rock-salt from Wieliczka; II. White, and III. Yellow rock-salt from Berchtesgaden; IV. From Hall in the Tyrol; V. Detonating salt from Hallstadt; VI. From Schwäbischhall.

	I.	II.	III.	IV.	V.	VI.
Sodium chloride . .	100·00	99·85	99·93	99·43	98·14	99·63
Potassium „ . .	—	—	—	—	traces	0·09
Calcium „ . .	—	traces	—	0·25	—	0·28
Magnesium „ . .	traces	0·15	0·07	0·12	—	—
Calcium sulphate .	—	—	—	0·20	1·86	—
	100·00	100·00	100·00	100·00	100·00	100·00

The so-called detonating salt, found at Wieliczka in crystalline-granular masses, has

the property when being dissolved in water of giving rise to slight detonations, accompanied by an evolution of hydrocarbon gas from microscopically small cells, the walls of which, becoming thin when the salt is dissolved in water, give way, and cause the report. If the solution of the salt takes place naturally in the mine, the gas partly escapes, and partly becomes condensed, forming petroleum, often met with in beds of rock-salt. The minerals of the salt deposit of Stassfurt are, according to MM. Bischof, Reichardt, Zincke, and others, the following:—

——	Chemical Formula.	In 100 parts are contained:	Sp. gr. of the compound.	100 parts of water dissolve at 18° C.	Synonyms and Observations.
Anhydrite	$CaSO_4$	100 of Sulphate of lime	2·968	0·20	Karstenite
Boracite	$B_{16}O_{30}Cl_2Mg_7$	26·82 Magnesia 65·57 Boric acid 10·61 Magnesium chloride	2·9	Almost insoluble	Stassfurtite
Carnallite	$KMgCl_3 + 6H_2O$	26·76 Chloride of potassium 34·50 Magnesium chloride 38·74 Water	1·618	64·5	Contains Bromine
Red oxide of iron	Fe_2O_3	100 of Oxide of iron	3·35	Insoluble	—
Kieserite	$MgSO_4 + H_2O$*	87·10 Sulphate of magnesia 12·90 Water	2·517	40·9	Martinsite?
Polyhalite	$2CaSO_4 MgSO_4 K_2SO_4 2H_2O$	45·18 Sulphate of lime 19·93 Sulphate of magnesia 28·90 Sulphate of potassa 5·99 Water	2·720	Is decomposed while being dissolved	—
Rock-salt	NaCl	100 Chloride of sodium	2·200	36·2	—
Sylvin	KCl	100 Chloride of potassium	2·025	34·5	—
Tachhydrite	$CaCl_2 2MgCl_2 12H_2O$	21·50 Chloride of calcium 36·98 Chloride of magnesium 41·52 Water	1·671	160·3	—
Kainite	$K_2SO_4 MgSO_4 MgCl_2 6H_2O$	36·34 Sulphate of potassa 25·24 Sulphate of magnesia 18·95 Magnesium chloride 19·47 Water	—	—	Contains Bromine
Schönite or Pikromerite	$K_2SO_4 MgSO_4 6H_2O$	43·18 Sulphate of potassa 29·85 Sulphate of magnesia 26·97 Water	—	—	—

Sylvin is also found in large quantities in the salt deposit near Kalucz, Galicia.

Mode of Working Rock-salt.—Rock-salt, like other minerals and according to its mode of occurence, is either quarried or mined. If it happens, however, that the rock-salt is mixed with other minerals, clay, gypsum, dolomite, &c., a solution in water is effected, which is pumped up from the mine as a concentrated brine. In many instances rock-salt is wrought in extensive and deep mines, as in the celebrated rock-salt mines of Wieliczka.

* According to Rammelsberg it is probable that kieserite is originally an anhydrous mineral, a conclusion which seems justified by the variable quantity of water found in different analyses.

Mode of Working Salt-springs.—Natural salt-springs sometimes occur, and these have been imitated artificially by boring to a great depth into layers of earth containing saline deposits. In this manner a brine may be obtained sufficiently concentrated to be at once boiled down. The method of working the natural salt-springs is to form a convenient reservoir from which the saline solution is immediately pumped up for the purpose of being gradated (see p. 168). The solution previous to being boiled down is left to allow the suspended matter to settle. The salt-springs obtained by boring either yield a native brine, or the borings are carried into solid rock-salt and water caused to descend into the salt deposit. This artificial brine is then pumped up, unless there is naturally an artesian formation. The brine previous to further operations is left for some time in reservoirs to deposit suspended insoluble matter.

These saline solutions are not always free from impurities; in considering their admixture brines may be divided into two classes; the first containing sulphate of magnesium or sodium, with chloride of magnesium; the other class embraces brine containing the chlorides of calcium and magnesium. If the brine happens to pass through peaty soil or layers of lignite, there often accrues organic matter, humic, crenic, and apocrenic acids.

Preparation of Common Salt from Brine.—This operation is duplex and consists in—

a. Concentrating the brine.
 α. By increasing the quantity of salt.
 β. By decreasing the quantity of water.
b. The boiling down of the concentrated brine.

Concentrating the Brine.—Native brines or salt springs seldom contain enough common salt to make it profitable to boil them down at once; it is consequently necessary to enrich the brine, and this may be done either (*a*) by dissolving in it rock-salt or crude sea-salt, neither being suited for culinary and many other purposes unless refined, or (*β*) by decreasing the quantity of water without the use of fuel.

Enriching by Gradation.—The enriching or concentration of a brine by decreasing the quantity of water it contains is called a gradation process, and may be proceeded with by freezing off the water in winter time, or more generally by evaporating the water by a true gradation process; either—(*a*) Gradation by the effect of the sun's rays; (*b*) Table gradation; (*c*) Roof gradation; (*d*) Drop gradation.

Gradation by means of the sun's rays is obviously the same method of procedure as that described under the treatment of sea-salt. Table gradation has been only experimentally tried at Reichenhall, and consists simply in causing the brine to flow slowly from a reservoir down a series of steps, constructed so as to give as much surface as possible, and thus hasten the evaporation. Roof gradation is effected by utilising the roofs of the large tanks containing the brine as evaporation surfaces, by causing the contents of the tanks to flow in a thin but constant stream over the roofs, which, of course, are exposed to the open air.

Faggot Gradation.—This operation, also known as drop gradation, is carried on by means of the following apparatus, termed a gradation house, and consisting of a framework of timber, fitted with faggots of the wood of *Prunus spinosa*, which being thorny, presents a large surface. The entire construction is built over a water-tight wooden tank, which receives the concentrated brine, and frequently the top of the gradation house is provided with a roof. Under the roof and above the faggots a water-tight tank is placed containing the brine to be gradated; this tank is provided with a number of taps, from which the brine trickles into channels provided with holes to admit of the brine falling on the faggots. These taps are placed on both sides of the gradation house, and are generally connected with levers to admit of being readily turned on and off from below. The gradation process is continued until the brine is

sufficiently concentrated to admit of being further evaporated by the aid of fuel; the brine may be gradated to contain 26 per cent. of salt, but the operation is rarely carried so far.

The gradation process not only serves the purpose of concentration, but also that of purifying the brine, as some of the foreign salts are deposited on the faggots; this deposit of course varies in composition according to the constituents of the brine, but chiefly consisting of calcium carbonate, with the potassium, sodium, and magnesium sulphates. The deposit has in some instances been used as manure. In the tanks where the gradated brine is collected another slimy deposit is gradually formed, consisting of gypsum and hydrated oxide of iron. As in the present day the brine obtained from bored wells is generally sufficiently concentrated to be at once boiled down, gradation is less frequent, being a very slow process and involving a loss of the salt carried off by the wind.

Boiling down the Brine.—The object is to obtain with the least possible expenditure of fuel the largest quantity of pure dry salt. Formerly the evaporation was carried on in large cauldrons, but at the present time evaporating vessels are constructed of well rivetted boiler-plate, the shape being rectangular, the length 10 metres, depth 0·6 metre, and width from 4 to 6 metres. These pans are supported by masonry, which also serves to separate the flues. Over the pans a hood is fixed and connected with a tube carried to the outside of the building to afford egress to the steam. The brine, concentrated to contain from 18 to 26 per cent. of salt, is poured into the pans to a depth of 0·3 metre.

The boiling down process is in many salt works conducted in two different operations:—

a. The evaporation of water to produce a brine saturated at the boiling point.

b. The boiling down of the saturated brine until the salt crystallises out.

The boiling down is generally carried on for several weeks, the scum being removed, together with the gypsum and sodium sulphate deposited at the bottom of the pan, with perforated ladles. As soon as a crust of salt is formed on the surface of the liquid, a temperature of 50° is maintained. At this stage the salt is gradually deposited at the bottom of the pan in small crystals, and being removed, is put into conical willow baskets, which are hung on a wooden support over the pan to admit of the mother-liquor being returned to it. Finally, the salt is dried and packed in casks.

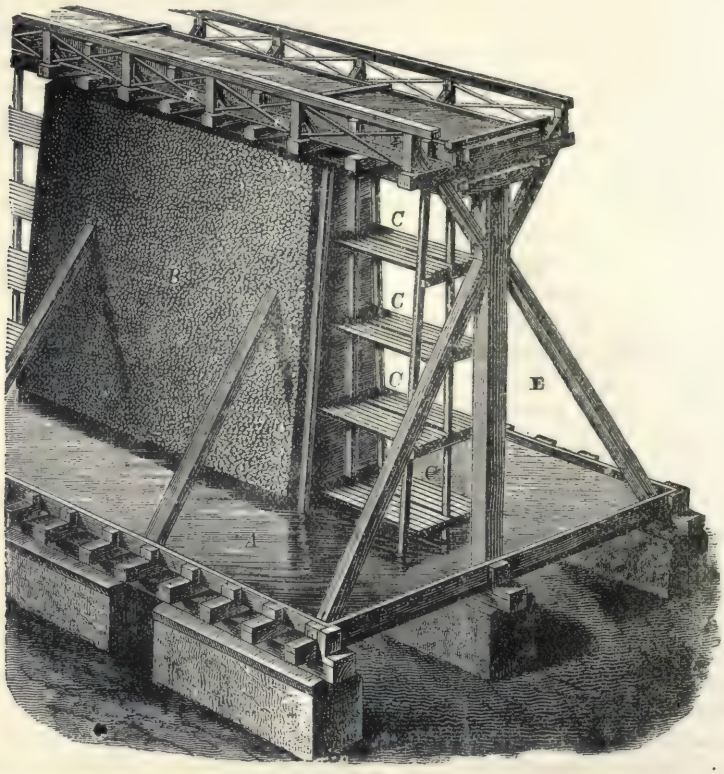
The quantity of mother-liquor collected after boiling for some two or three weeks is, compared with the quantity of brine evaporated, very small; it was formerly thrown away or used for baths, but is now employed for the preparation of potassium chloride, the sodium and magnesium sulphates, artificial bitter water, and in some instances for preparing bromine. It is evident that by the boiling down all the salt contained in the brine is not obtained as dry refined salt, a portion being retained among the early deposit formed at the bottom of the pan, another portion remaining in the mother-liquor, and finally some loss accrues from the nature of the operations, amounting generally from 4 to 9·25 per cent.

Properties of Common Salt.—Sodium chloride crystallises in cubes, the size of the crystals determining the varieties known in the trade as coarse, medium, and fine grained salt, and depending upon the rate of evaporation of the brine, a slow evaporation producing very coarse salt. Perfectly pure common salt is not hygroscopic, but the ordinary salt of commerce contains small quantities of magnesium chloride and calcium. Usually, salt contains from 2·5 to 5·5 per cent. of water, not as a constituent, but as an intermixture; hence the phenomenon called decrepitation, due to the breaking up of the crystals by the action of the steam when salt is heated. Ignited to a strong red heat sodium chloride fuses, forming an oily liquid, and at a strong white heat is volatilised without decomposition. Common salt is readily soluble in water, and is

one of the few salts almost equally soluble in cold and in hot water; 100 parts of water at 12° dissolve 35·91 parts of common salt.

In order to express the quantity of salt contained in a brine, it is usual to say the brine is of a particular fineness, strength, or percentage; for instance, a brine at 15 per cent. contains in 100 parts by weight 15 parts of salt and 85 parts of water. The *Grädigkeit* or degree of a brine means the quantity of water which holds in solution

Fig. 281.



1 part by weight of salt; a brine of 15·6 *Grädigkeit* contains, therefore, 1 part by weight of common salt in 15·6 parts of water. The poundage (*Pfündigkeit*) of a brine indicates in pounds the quantity of salt contained in a cubic foot of brine. The following table shows the percentage of salt contained in brines of the several specific gravities:—

Salt per cent.	Sp. gr.	Salt per cent.	Sp. gr.	Salt per cent.	Sp. gr.
1	1·0075	7·5	1·0565	16	1·1206
1·5	1·0113	8	1·0603	17	1·1282
2	1·0151	8·5	1·0641	18	1·1357
2·5	1·0188	9	1·0679	19	1·1433
3	1·0226	9·5	1·0716	19·5	1·1510
3·5	1·0264	10	1·0754	20	1·1593
4	1·0302	10·5	1·0792	21	1·1675
4·5	1·0339	11	1·0829	22	1·1758
5	1·0377	11·5	1·0867	23	1·1840
5·5	1·0415	12	1·0905	24	1·1922
6	1·0452	13	1·0980	25	1·2009
6·5	1·0490	14	1·1055	26·39	1·2043
7	1·0526	15	1·1131	—	—

Uses of Common Salt.—It is not necessary to enter into particulars on this subject. Salt is used as a necessary condiment to food; a man weighing 75 kilos. contains in his body 0·5 kilo. of common salt, and requires annually 7·75 kilos. to maintain this supply. Common salt is used in agriculture, and is as necessary for cattle and horses as for man. It serves industrially in the preparation of soda, chlorine, sal-ammoniac, in tanning, in many metallurgical processes, the manufacture of aluminium and sodium. Further, it is employed in the glazing of the coarser kinds of pottery and earthenware, from the fact that when common salt is fused with a clay containing iron, the sodium is oxidised and forms soda, which, combining with the alumina and silica, supplies a glaze, while the iron combining with the chlorine is volatilised. The uses of common salt for the preservation of wood, for curing meat, preserving butter, cheese, &c., are too well known to require explanation. Among the salt-producing countries of Europe, England takes the lead, producing annually 32,400,000 cwts., while Germany only produces 10, and Russia 20 million cwts.

Fig. 281 shows an apparatus used for concentrating brine from salt springs, &c., without the use of artificial heat. It consists of a stout frame work of beams, *C*, supporting a system, *B*, of faggots of thorns, &c. At the bottom is a water-tight tank for receiving the brine.

In countries where a tax upon salt still exists the following substances are officially added to salt used for technical purposes, so as to render it unfit for domestic uses: in alkali works 4 to 15 per cent. of soda-ash, 12 per cent. of soda crystals, sulphuric acid (about 2 per cent. with 3 to 4 parts of water), 10 per cent. sodium bicarbonate, ammonia, 5 to 16⅔ per cent. Glauber salts. In other chemical and in colour works: anilin colours and decoctions of dyes; iodine lye, mother-liquors from extract of indigo, 5 per cent. copper chloride, ¾ per cent. red lead, &c., and a variety of other products.

SODA.

Soda is either (A) natural soda, or (B) that from plants and sea weeds, or (C) that obtained by chemical processes from the sodium compounds occurring in nature (such as common salt, Glauber salt, soda-saltpetre, cryolite) with the simultaneous production of hydrochloric acid, chloride of lime, sulphur, sal-ammoniac, potassium nitrate, alum, aluminium sulphate, sodium aluminate and thio-sulphate.

(A) Natural Soda.

Soda occurs naturally as an ingredient in many mineral springs, it weathers out volcanic rocks, *e.g.*, trass and gneiss, as at Bilinboth, as sodium sesquicarbonate $Na_2CO_3 + 2NaHCO_3 + 2H_2O$, or as sodium pyrocarbonate, and often exists in solution in the so-called soda-lakes. Such waters exist in Egypt in the western part of the Delta, in Central Africa, in the plains along the Caspian, in California, Mexico, and in some South American States. In the great Hungarian plain crude soda weathers out during the hot season as a saline crust, which is collected for sale. The Egyptian soda is known as Tro-Na, whence the name Natron, still used for soda in Germany. It is exported yearly from Alexandria to the extent of 5000 tons. In Columbia soda, called there Urao, is deposited in the hot season at the bottom of a lake in the valley.

La Lagunilla.—In La Plata (province Catamanca) soda is found in great quantities, and is known as Ccollpa. Quite recently an alleged inexhaustible bed of natural soda has been found in Virginia.

The sodium carbonate of the alkaline lakes is probably formed on the decomposition of common salt by means of calcium or magnesium bicarbonate; or it may be produced from sodium sulphate which is reduced to sodium sulphide by the action of organic

matter. The sulphide is then converted into sodium sesquicarbonate by means of carbonic acid dissolved in the water.

(B) Soda from Plants.

As inland plants take up from the alkalies of the soil principally potash, which is found in the ashes of such plants in the state of carbonate, so plants growing on the coast, in the sea itself, or in salt-steppes, contain more or less sodium, combined with sulphuric acid or with organic acids. Such plants, on incineration and lixiviating, yield sodium carbonate. Besides the species of fucus growing in the sea itself, the genera *Statice*, *Chenopodium*, *Mesembryanthemum*, *Salsola*, *Atriplex*, *Salicornia*, &c., serve for the production of soda and in some districts are even cultivated. The plants are mown, the kinds of fucus are collected at ebb-tide and dried on the shore. The plants are then burnt to ashes in pits. The heat is so strong that the ash melts, and on cooling forms a hard, brownish-grey slag-like mass known as crude soda or soda-ash. It contains from 3 to 30 per cent. of sodium carbonate. It is worked up by lixiviating and concentrating the lye. The following kinds are distinguished according to their origin and the manner of their production:

a. Barilla soda, from Alicante, Malaga, Cartagena, the Canaries, &c. It is obtained from the Barilla (*Salsola* soda) which is cultivated on the coasts of Spain. It contains from 25 to 30 per cent. of sodium carbonate.

b. Salicor soda, from Narbonne, obtained by burning *Salicornia annua*, a plant which is sown and reaped after the seed is ripe; it yields about 14 per cent. of sodium carbonate.

c. Blanquette soda, from Aigues-Mortes, from plants grown between Aigues-Mortes and Frontignan, *Salicornia Europæa*, *Salsola kali*, *Statice limonium*, *Artiplex portulacoides*, &c. It contains only from 3 to 8 per cent. of sodium carbonate.

d. Equal in value to Blanquette soda is Araxes soda, much used in South Russia, and obtained in Armenia in the Schurus direct on the table-lands of the Araxes.

e. Still poorer is the Varec soda, Tang soda, obtained in Normandy and Brittany from various sea-weeds, especially the *goëmon*, *Fucus vesiculosus*.

f. About equal in value to Varec soda is kelp, obtained on the western coasts of the British Islands (Scotland, Ireland, Orkneys), from various kinds of salsola, and sea-weeds (*Fucus serratus* and *F. nodosus*, also *Laminaria digitata*); here and there it is obtained from sea-grass (*Zostera maritima*).

g. Lastly is to be mentioned the soda derived from the beet, which always contains a few per cents. of potassium carbonate.

(C) Soda obtained by Chemical Means.

The numerous attempts made at first by French chemists to obtain from common salt a soda equal to barilla in cheapness and quality led to no results, and the large rewards offered by the Academy of Sciences for the solution of the problem were not claimed. When, in consequence of the revolutionary war the importation of soda and potash was broken off, and when all the potash which France produced was required for the manufacture of saltpetre and gunpowder, the Committee of Public Welfare demanded the most accurate returns concerning all soda manufactories, Leblanc was one of the first manufacturers to obey this call, and he handed over for the public use the principles on which he was on the point of erecting a soda-works. His process was declared the most suitable, and until the recent introduction of the ammonia process it has been in almost exclusive use.

1. *The Leblanc Process.*—This process consists essentially in the production of sodium sulphate, its fusion with lime and coal, and the purification of the crude soda; after this follows the treatment of the residues.

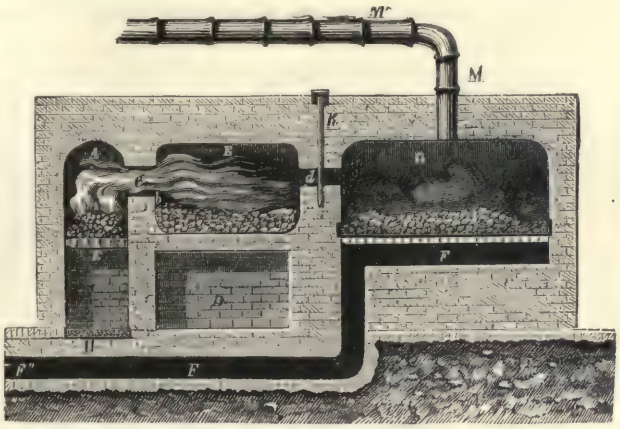
a. The production of sulphate (salt-cake) from common salt is generally effected by means of chamber acid, according to the equation:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The decomposition was at first effected in open reverberatories, so that the hydrochloric acid escaped mixed with the gases of combustion.

In 1836 Gossage obtained a patent for a closed reverberatory, which during the first part of the decomposition acted as a distilling apparatus, and subsequently, being heated by direct firing, it acted as an open furnace in order to complete the conversion of the salt into salt-cake. By combining this furnace with coke towers as coolers, he succeeded in obtaining in the first section a strong acid fit for the production of chloride of lime, and then a weaker acid. This furnace was decidedly improved by Gamble in 1839; at least he seems to have been the first who caused the two portions of the decomposition to take place in two distinct compartments of the furnace *G* and *E* (Fig. 282). The principle of this furnace was universally adopted, and for some time the alkali manufacturers made use of a reverberatory which by opening or shutting an aperture could be connected with a kind of muffle, the bottom of which consisted of a strong iron plate. The flame, after heating the reverberatory, played round the muffle and then up the chimney. The muffle itself was connected by *M* with a condensing apparatus which yielded concentrated hydrochloric acid. On this principle the salt was let fall upon the cast-iron sole of the plate, G, and the acid, previously heated, is allowed to flow in. A brisk reaction was set up, and half, or nearly $\frac{2}{3}$ of the acid escaped and could be easily condensed, as it was not mixed with the gases of the fire. The product obtained was a mixture of sodium bisulphate with common salt—

Fig. 282.



$$2NaCl + H_2SO_4 = NaHSO_4 + NaCl + HCl,$$

and was drawn into the reverberatory, *E*, whilst *G* received a new charge of salt and sulphuric acid. In the reverberatory, which was much hotter than the muffle, the mixture of salt and bisulphate was converted into hydrochloric acid and neutral sulphate: $NaHSO_4 + NaCl = Na_2SO_4 + HCl$.

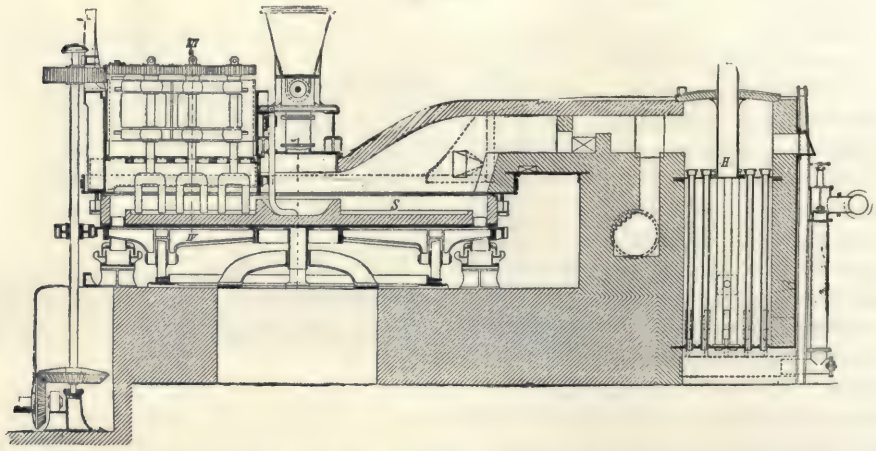
The hydrochloric acid evolved was difficult to concentrate, as it was mixed with nitrogen, carbon dioxide, and carbon monoxide. In spite of the scrubber, a part of the hydrochloric acid escaped into the air and there were required very large apparatus and especial precautions in order to effect a satisfactory condensation.

These difficulties are nearly overcome since the salt-cake furnaces have been improved as follows. The new furnace consists of two muffles, one of iron and one of brick. A part of the sole forms a shallow cast-iron basin 2·74 metre in diameter and 0·52 metre in depth; it stands on a foundation of bricks and is provided with a cast-iron cover, which is likewise a segment of a sphere of 0·30 metres in depth. In this cover there are two apertures closed by doors, the one for introducing the salt, whilst the mixture is conveyed into the brick muffle through the other. The fire is at the side of the cast-iron muffle,

and its flame acts first upon the cover and then upon the basin. The brick muffle is next to the iron muffle, and is a chamber of 9·14 metres in length, and 2·74 metres in width. Beneath its brick sole there is a series of flues; its upper part consists of a thin vault of brick supporting a second vault, and the flame circulates in the space between both. At one of the sides of the brick muffle is a fire, the flame of which passes first between the two vaults and then through the flues beneath the sole. In this manner the heat passes through the masonry of the vault and the floor to the mixture of bisulphate and salt in the muffles.

In working with this apparatus 500 kilos. of salt are placed in the iron muffle, previously heated, and the requisite quantity of acid at sp. gr. 1·7. The mass is stirred up from time to time. It gradually thickens, and in about 1½ hour (after ⅔ of the hydrochloric acid have escaped) it is so solid that it can be removed into the brick muffle, which is kept at a bright red heat, so that the hydrochloric acid may entirely escape. There is an arrangement for cutting off the connection between the two muffles, so that the gases escaping from either may be received separately.

Fig. 283.



The salt-cake furnaces of Jones and Walsh are used for sodium sulphate at Aussig, as well as in Britain, and by Vorster and Grüneberg at Cologne for potassium sulphate. Opinions on them differ.

In the sulphate furnaces of Mactear the salt and sulphuric acid flow uninterruptedly into a pan formed by a ring-shaped prominence in the sole of the furnace. The mass, whilst still thin, flows over into the part of the hearth *S* (Fig. 283) situate nearest the middle, where the decomposition is carried on about as far as the formation of bisulphate. By the position of the agitator the mass is gradually brought towards the outside and further decomposed, so that the outer part of the hearth plays the part of a calcining furnace. At first Mactear arranged the hearth of the furnace in concentric rings, but he has given up this idea. The removal of the gases of combustion, which are of course mixed with the vapours of sulphuric acid, is effected by a cast-iron pipe on each side of the agitating apparatus. The vault is made to descend, and the entire arrangement is such—as may be seen from the illustration (Fig. 283)—that the agitating apparatus can suffer little from the heat. The sole of the furnace is lined with fire-clay tiles which have been boiled in tar: for mortar there is used a cement which becomes continually harder by the action of the heat and the sulphate, so that the entire sole bakes together to a solid mass, which effectively resists the action of the charge. The heating is effected as may be convenient, but of course in such a manner that no such flame arises as would choke the condensers. Recently Mactear has made use of four

Wilson gas-generators, between which and the furnace is interposed an iron superheating apparatus, *H*.

The process of producing salt-cake and hydrochloric acid devised by Hargreaves and Robinson has been known since 1872, and is in action on the large scale in a number of English works. It consists in the direct action of sulphurous acid (the gases from roasting pyrites), oxygen (atmospheric), and watery vapour upon sodium chloride—

$$SO_2 + O + H_2O + 2NaCl = Na_2SO_4 + 2HCl.$$

The sodium chloride gives the best results when it is very finely divided before being formed into lumps. It is moistened and dried, when it takes the condition of hard, flat cakes, which are broken into fragments of about 38 millimetres in diameter. By adding a little sulphate to the water the pieces are rendered harder and more suitable. The pieces of salt come upon an iron grating placed near the floor in cylindrical chambers of a fire-proof material. They are there treated at a red heat with a mixture of two vols. of sulphurous acid, two vols. of watery vapour, and so much air that its oxygen may represent one vol. The gaseous mixture enters below the iron grating; the temperature rises by the heat of the reaction, so that the gaseous hydrochloric acid escapes very hot; it is drawn into coke towers and there absorbed by water. The process is uninterrupted, and as a rule eight cylinders are used simultaneously. In place of the chambers, a tower is used built of fire-proof stone and provided at bottom with a grating, through which the gases enter. The pieces of salt are introduced from above and the salt-cake as it is formed is withdrawn below. The advantages of the Hargreaves process lie in the dispensing with sodium nitrate, the production of a sulphate of very high grade (free from undecomposed salt), decrease of the escape of gases, continuous development and ready condensation of the hydrochloric acid, reduced loss of sulphur, and consequently greater yield. Its defects are, increased cost of installation, greater consumption of fuel, and increased outlay for labour.

Hydrochloric Acid.—The liquefaction of hydrochloric acid by water is effected the more easily and completely the less the HCl is mixed with combustion gases, &c., and the lower the temperature of the water; one gramme of water at the pressure of 760 millimetres disssolves—

Temperature.	HCl.	Temperature.	HCl.
0° ...	0·825 grm.	24° ...	0·700 grm.
4 ...	0·804 „	28 ...	0·682 „
8 ...	0·783 „	32 ...	0·665 „
12 ...	0·762 „	36 ...	0·649 „
16 ...	0·742 „	40 ...	0·633 „
20 ...	0·721 „	44 ...	0·618 „

The vapours of hydrochloric acid are passed through a number of earthenware vessels in the opposite direction to the water, so that the solution when nearly saturated comes in contact with the strongest gases; or the vapours are led through towers built of bricks soaked in tar, or stone plates, the filling of which (coke or stones) is kept constantly moistened with water.

Properties.—Hydrochloric acid forms a colourless liquid, frequently coloured yellow by ferric chloride or organic matter, and having a pungent odour. At 20° water absorbs 475 times its own volume of hydrochloric acid gas; the saturated solution contains 42·85 per cent. of HCl and its sp. gr. = 1·21. According to J. Thomson (1874), hydrochloric acid probably contains a hydrate of the composition $HCl.H_2O$, which must be regarded as the true molecule of the acid. The following table shows th sp. gr. of hydrochloric acid of different strengths and its percentage of actual acid (at 7°):—

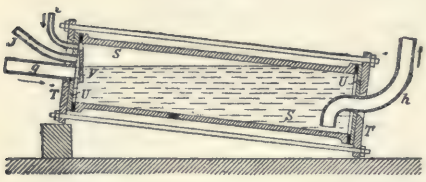
Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Percentage of Acid.	Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Percentage of Acid.
1·21	26	42	42·85	1·10	14·5	20	20·20
1·20	25	40	40·80	1·09	12	18	18·18
1·19	24	38	38·88	1·08	11	16	16·16
1·18	23	36	36·36	1·07	10	14	14·14
1·17	22	34	34·34	1·06	9	12	12·12
1·16	21	32	32·32	1·05	8	10	10·10
1·15	20	30	30·30	1·04	6	8	8·08
1·14	19	28	28·28	1·03	5	6	6·06
1·13	18	26	26·26	1·02	3	4	4·04
1·12	17	24	24·24	1·01	2	2	2·02
1·11	15·5	22	21·22				

The author remarks in a note that Twaddell's hydrometer scale, used in England, possesses the noteworthy feature that the degrees coincide with tolerable exactness with the percentages of acid.

Applications.—The production of a non-arsenical hydrochloric acid is easily effected by distillation with ferrous chloride, when the arsenic—the more readily the greater its strength—passes over in the first portions of the distillate. An acid of 30 to 40 per cent. is mixed with a little ferrous chloride, the first 30 per cent. which pass over are set aside as arseniferous, and the 60 per cent. which follow next, and are pure, are collected separately. In this manner an acid of 20 to 30 per cent. is obtained. The process s adapted for the industrial production of a non-arsenical acid, in as far as the crude acid generally containing ferric chloride needs merely to be mixed with a few iron turnings and submitted to fractional distillation.

Hydrochloric acid is used on a vast scale for the production of chloride of lime, potassium chlorate, and other chlorine preparations (*e.g.*, chloral hydrate, chloroform, chlorbenzyl, benzotrichloride, methyl chloride); it serves also in the manufacture of sal-ammoniac, antimony chloride, glue, and phosphorus; in the production of carbon dioxide (for the mineral water trade); in the manufacture of alizarine, resorcine, and salicylic acid; in the preparation of sodium bicarbonate; in purifying bone black for sugar works; in bleaching as a substitute for sulphuric acid; in converting saccharose into a fermentible invert-sugar; in working up beet treacle into alcohol; in the production of ammonia and methyl chloride from the dregs of beet treacle; in the metallurgy of copper, nickel, cadmium, zinc, and bismuth; for dissolving metals (tin), either alone or when mixed with nitric acid as aqua regia; for purifying ferruginous sands for the glass manufacture; for carbonising wool. An important use of hydrochloric acid occurs in the cotton manufacture—*i.e.*, for decomposing the lime-soap which is formed when cotton tissues impregnated with fatty matters are bowked with lime. Hydrochloric acid was formerly sold in glass carboys or stoneware jars (often of more value than their contents). Sometimes it is sent out in casks, lined with a layer of gutta percha 1 centimetre in thickness.

Fig. 284.



For raising hydrochloric acid Kestner uses a stoneware cylinder, *S*, with cast-iron covers, *T* (Fig. 284), screwed together with iron rods. The cover, *U*, is formed of vulcanite, and the valve, *V*, of caoutchouc. The acid flows in by the tube, *g*, and is forced outwards through *h*; the compressed air enters at *i* and escapes during filling by the pipe, *j*. An apparatus of this kind, holding 50 litres, lifts hourly 2500 litres of acid to the height of 15 metres.

Sodium Sulphate, often called simply sulphate. ($Na_2SO_4.10H_2O$), is chiefly formed

as an intermediate product by the decomposition of common salt by sulphuric acid in the Leblanc process. It occurs naturally in the minerals thenardite, Na_2SO_4, brogniartin or glauberite, $Na_2SO_4.CaSO_4$, and astrakanite, $Na_2SO_4.MgSO_4.4H_2O$, in many mineral waters, in sea-water, and in most lime springs. The sulphate, as it is produced in the alkali works as salt-cake, contains on an average 93 to 97 per cent. dry sodium sulphate, and 2 to 3 per cent. sodium chloride.

Applications.—Sulphate is chiefly used in the manufacture of Leblanc soda, ultramarine, and glass. In the last case only the soda comes in question. It is fused with coal and quartz sand; by the action of the fuel the sulphuric acid of the sulphate is reduced to sulphurous acid ($Na_2SO_4 + C = CO + N_2SO_3$), which is driven out by the silica, and sodium silicate remains. For use in glass works salt-cake is previously purified from iron by dissolving the salt, precipitating the iron oxide by means of lime, evaporating down the clear solution, and drying the product. In the same manner water-glass may be formed from the sulphate by melting it with sand and carbon, and on the same principle sodium aluminate is obtained from the sulphate along with bauxite or aluminous earth. Considerable quantities of sulphate are also used in separating antimony from quartzy ores—*e.g.*, at Bouc and Septèmes, near Marseilles. Latterly, sulphate (freed from any excess of acid) has been used as an adjunct in dyeing, especially for wool.

Fig. 285.

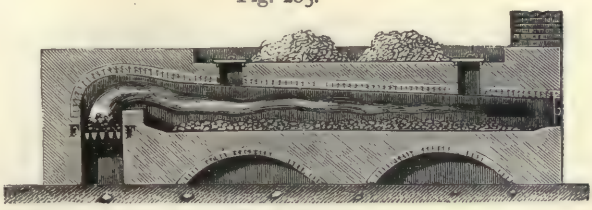


Fig. 286.

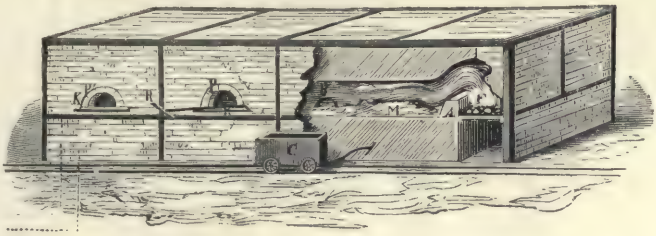
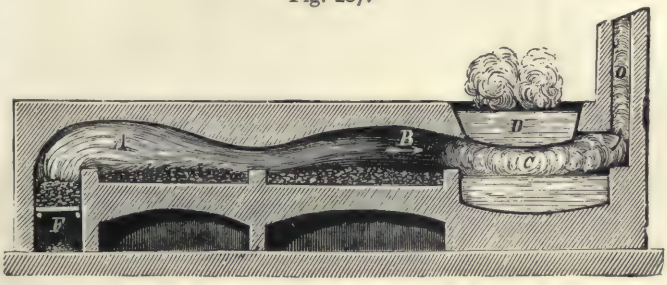


Fig. 287.



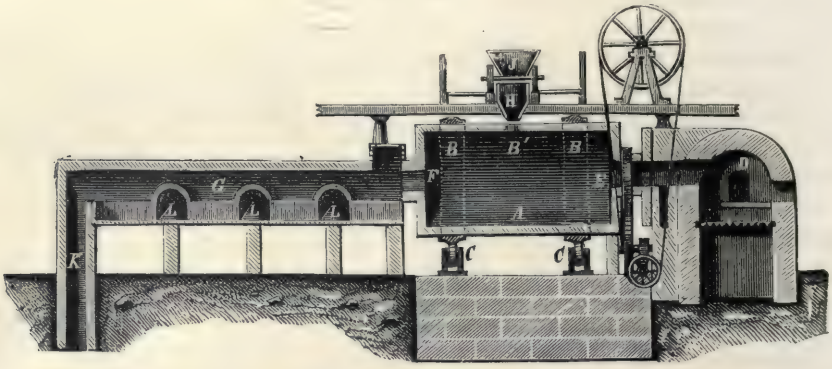
b. Conversion of Sulphate into Crude Soda.—The salt-cake is mixed with limestone (sometimes hydrated lime) and coal, and the mixture is melted upon the hearth of a reverberatory. The proportions given by Leblanc are: 100 parts salt-cake, 100 carbonate of lime, and 50 coal. In ten different establishments the proportion of limestone used to 100 parts of salt-cake ranges from 90 to 121 parts and the coal from 40 to 75. The lime of the lixiviated and desulphurised vat-waste is sometimes used as a substitute for natural calcium carbonate. In Britain reverberatories with two stages are often used (Fig. 285). The furnace was formerly charged with the materials ground and mixed. Now it is preferred to use them in fragments, in order that the soda "balls" may be sufficiently porous to admit of easy fracture and lixiviation. In Germany the furnaces have sometimes only one hearth (Fig. 286). In others, and in the English

works, the mixture which was prepared by the waste-heat in the upper stage remains only for half an hour on the lower hearth, which is the working-furnace. In German alkali works, the mixture, *M*, placed in the hot reverberatory, is heated until the mass is in a state of pasty flux, during which it is continually stirred with long iron rabbles, *K*. Bubbles of carbon monoxide burst out of the mass and burn with a blue flame. When the flames disappear the mass is drawn out of the furnace through the working doors, *P*, into flat sheet-iron chests on wheels, *C*, in which it cools.

As the combustion gases which escape from the hearth of the furnace have a very high temperature, a second hearth is placed behind the ordinary one, which serves for a preliminary heating of the next charge whilst the first charge is being completed. Fig. 287 shows such a furnace, with the two hearths, *A* and *B*, and there is here a third compartment, *C*, of the form of a pan, in order at the same time to effect the concentration of the soda-lye by the hot gases as they pass to the chimney, *O*. Above this compartment is the pan, *D*, in which the lye is concentrated before it is led into *C*.

The author has examined the temperature of the melted soda and the composition of the gases which are evolved. He found: 10 minutes after charging, a temperature of 713°; 20 minutes after, 15·7 per cent. carbon dioxide, 5·3 oxygen, temperature —; 40 minutes after, 18·1 carbon dioxide, 3·3 oxygen, temperature 779°; 55 minutes after, a temperature of 874°; 70 minutes after, and shortly before drawing the melt, carbon dioxide 15·8 per cent., oxygen 6.1, and the temperature 532°. 150 kilos. salt-cake, 160

Fig. 288.



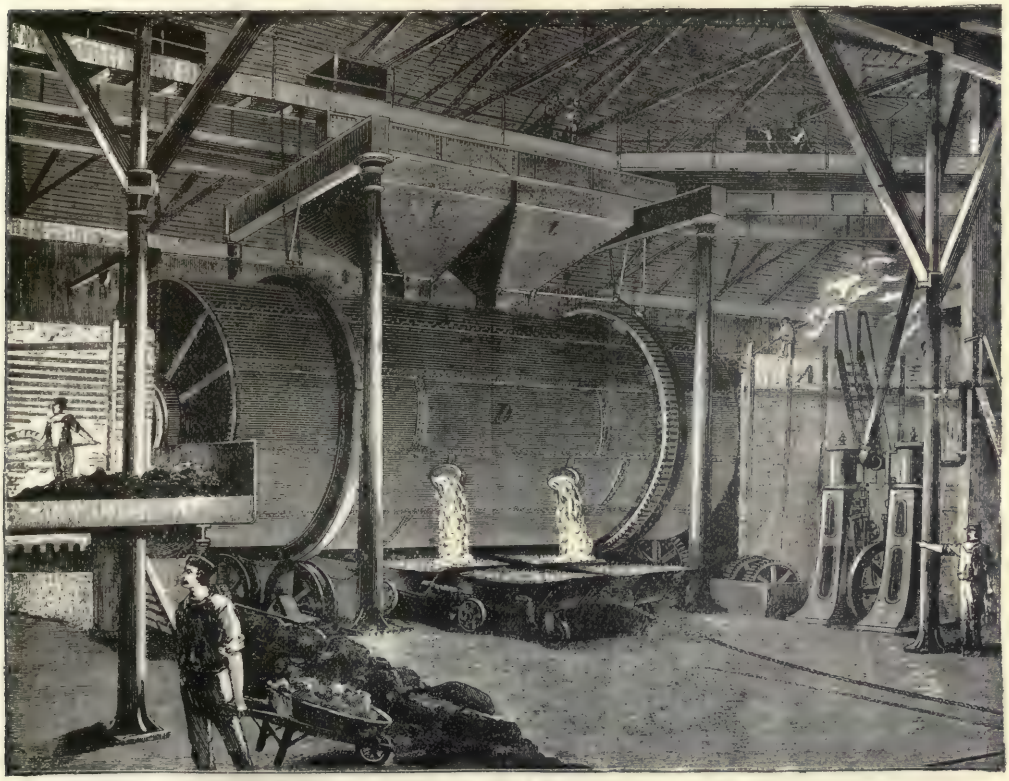
kilos. limestone, and 60 kilos. coal for reduction gave 240 kilos. crude black-ash with a consumption of 96 kilos. of coal. With another quality of coal only 42 kilos. were used for heating, and the carbon dioxide in the gases rose to 28 per cent.

In the furnace with a rotatory hearth this hearth consists of a cylinder which can be turned on its axle. The mixture of salt-cake, limestone, and coal is placed in the iron cylinder, *A* (Fig. 288), lined within with fire-stone. Two ribs, *B*, have been cast upon it, by means of which the cylinder rests upon two pairs of wheels, *C*. The one pair is provided with an axle, which communicates rotation to the wheels and from them to the cylinder. The fire-gases of the furnace, *D*, pass through the opening, *E*, into the cylinder, then through *F* into the vault, *G* (for the pans), and through the flue, *K*, to the chimney. After the interior of the cylinder has been heated to redness the mixture is brought upon a truck, *J*, and introduced into the cylinder by a hopper, *H*, which is not permanently connected. After the heat has acted for about 10 minutes upon the contents of the cylinder, the wheels are set in motion, and the cylinder is allowed to make a half-rotation. It is then let stand still for 5 minutes and another half-turn is taken. The operation is continued until the mass is melted, which takes place in about an hour. It is then set in rotation so as to turn once every three minutes.

The progress of the operation is watched from time to time by opening a door placed in the cylinder. When the process is complete the melt is allowed to flow into iron vessels placed below. The openings, *B*, *B*, serve for filling and emptying.

The rotating soda-furnace, or revolver, is an instance of the widely felt need to substitute mechanical appliance for costly manual labour. The idea of producing crude soda in a rotatory apparatus is due to Elliot and Russell. They experimented with several furnaces constructed at the machinery works of Robinson, Cookes, and Co., of St. Helens. The real difficulties were first overcome by J. C. Stephenson, at the works of the Jarrow Chemical Co., of South Shields. The first revolver was supplied to the company by Cookes, of St. Helens, in 1854, but it was not until 1868 that the first larger apparatus was introduced by Gaskell, Deacon, and Co., of Widnes, and by A. G.

Fig. 289.



Kurtz, of St. Helens. From that time these apparatus have been introduced into almost all British alkali works. The largest revolver hitherto built has been recently erected by the above-named machinery works of St. Helens for the Widnes Alkali Co., of Widnes. It does the work of 18 hand-furnaces, but only takes up the room of three such. Its daily yield is 80 to 90 tons of black-ash. The fire, *F* (Fig. 312), covers a space of 5·1 by 3·1 metres, and uses hourly 1·27 tons of coal. The revolver, *D*, consists of a wrought-iron cylinder, lined with fire-stone, and provided with two bearing rings of steel, which rest upon four small wheels. It is set in motion by two small steam engines mutually connected, the movement being transferred by means of toothed wheels. Above it are the hoppers *t*, and behind it evaporating pans for utilising the waste heat.

Whilst the earlier revolving furnaces of about $5\frac{1}{2}$ metres long work up each time 4 tons of salt-cake and require 650 kilos. of coal per ton, this furnace requires only 500 kilos., and yet the escaping gases suffice to concentrate so much lye of 20 up to 50° Tw. that it can supply three special caustic soda pans, representing an economy of fuel of 80 tons weekly. The revolving furnace is 9 metres long, with an inside diameter of 3·4 metres, and has three doors for filling and emptying. It is lined with 16,000 ordinary fire-stones and 120 weighing each 63 kilos. In seven days 400 tons of salt-cake are worked up to 240 tons of a 60 per cent. caustic soda, with the consumption of 200 tons of coal.

Crude soda (black-ash) has approximately the following composition :—

Sodium carbonate	45
Calcium sulphide	30
Caustic lime	10
Calcium carbonate	5
Foreign matter	10

There are sometimes formed in the black-ash crystals of a complex calcium sulphide-alumina-lime silicate, $2CaS.6Ca_3SiO_5.Al_3SiO_5$, as also of the silicate, $Ca_3Si_2O_7$. About 5 per cent. of the sodium forms insoluble compounds.

Considerable quantities of crude soda, especially in England, are used without further treatment in soap-making, in bleaching, and in the manufacture of bottle-glass.

c. Conversion of Crude Soda into Purified Soda, by Lixiviation and Evaporation.—Crude soda is resolved by extraction with water into a solution of sodium carbonate and an insoluble residue (tank-waste, vat-waste, soda-waste, and sometimes, erroneously, black-ash !)

The blocks of English crude soda are in general of a darker colour and richer in coal than those from Continental works. Before lixiviating they are generally exposed to the air for one or two days, in some places ten to twelve days, not merely to let them cool but that they may partially weather, thus rendering the subsequent treatment more easy. As J. Kolb has observed, crude soda during weathering undergoes the following changes :—The exposure of crude soda to a perfectly dry air does not, as long as it lasts, notably alter its composition ; if it contains, on being burnt, sodium sulphide, it may be improved to a certain extent, as the sulphate passes into thiosulphate. At 100° dry air seems also without action upon crude soda, but as the temperature rises, and especially if it reaches redness, the calcium sulphide is converted into calcium sulphate, which lessens the standard of the soda, since during lixiviation it enters into double decomposition with sodium carbonate, forming sodium sulphate. According to Pelouze, a reduction of the strength is to be seen even between 200° and 300°. Hence it is very important to promote cooling of the soda after its removal from the furnace, and to effect this with the exclusion of air in well-fitting trucks.

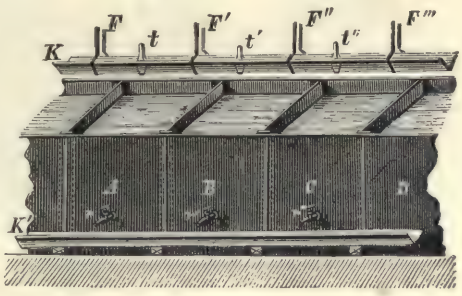
If crude soda is exposed to moist air ammonia is evolved in consequence of the decomposition of the sodium cyanide which is always present; the lime passes into hydrate, which expands in volume, and produces clefts in the blocks of soda, which then fall to pieces. The calcium hydrate passes slowly into carbonate, which reduces the proportion of caustic soda in the lye. At the same time the sodium sulphide (the presence of which is always indicated by red spots) is oxidised and becomes sodium thiosulphate. If there were no other reactions the exposure would be advantageous, but any favourable action is neutralised by the oxidation of the calcium sulphide. Moist air, like dry air, can, therefore, act favourably only in case of soda which is not burnt. If the causticity of a well-made crude soda is diminished by exposure, this is effected to the disadvantage of the proportion of alkali, which decreases in the same degree. Hence, the action of air should, generally speaking, continue only long enough for the lime to be partially hydrated, thus greatly facilitating the breaking

up of the raw soda. The time, according to the moisture of the air and the proportion of free lime in the soda, may vary from three to six days. A longer exposure is rarely without injury, and the custom of leaving the balls in the air for sometimes twelve days is to be condemned.

The oldest method of lixiviation consisted in grinding the crude soda, and stirring up the sifted powder with 4 parts of water. After the undissolved portion had settled the solution was poured off and brought into contact with fresh portions of crude soda, repeating this process three or four times. At the same time fresh water was poured upon the undissolved matter remaining in the first vat, and was gradually transferred from vat to vat. In this manner all the soluble constituents were removed from the crude soda. This method of lixiviation was open to several objections; the water exerted its solvent power only on stirring, and hence the quantities dissolved were never considerable. It further required much labour, and is, in consequence, no longer in use.

The method of lixiviation by simple filtration is also not to be recommended, on account of the great labour it requires. It consists in placing the crude soda in sheet-iron tanks provided with perforated false bottoms, and covering it with water. A series of tanks, *A*, *B*, *C*, *D* (Fig. 290), $1\frac{1}{2}$ metre high, 1·8 metre broad, and 2 metres long, are set close together on a platform of masonry. At $\frac{1}{4}$ metre from the bottom is a perforated false bottom of wood or sheet iron. A wooden main, *K*, placed above the tanks, and held by the irons, *F* and *F'*, leads the liquid into the tanks though the plugs, *t*, *t'*, and *t''*. In the latter there are fixed below the false bottom, the cocks, *r*, *r'*, *r''*, &c., which serve to run off the solution from the tanks into the channel, *K'*. The blocks of crude soda broken up into fragments of about the size of a head, are laid in the false bottom, where they are submitted to a repeated process of lixiviation. Suppose a system of three tanks, *A*, *B*, *C*, the tank *A* charged with fresh crude soda, *B* with such as has been once lixiviated, and *C* with some that has been twice lixiviated. We let flow into each through the channel, *K*, the last washings of a previous lixiviation. These washings have to stand eight hours in each. After the lapse of this time, the lye (which will mark about 50° Tw.) is let off through the cock, *r*, into the channel, *K*, as also the much weaker lyes from *B* and *C*, which are mixed in large tanks with the lye from *A*, and reduce its strength to about 40° Tw. Washing-waters are again run in upon *A* and *B*, and into a fourth tank, *D*, charged with fresh crude soda; after eight hours the lyes are run into the cistern, which has already received the lyes from the former working, &c. It is thus possible to obtain without interruption a lye of 40° Tw. After the contents of each tank have thus been lixiviated three times, the residues are finally washed with water at 50°. The liquid thus obtained serves to lixiviate the soda in the tanks, *A*, *B*, and *C*.

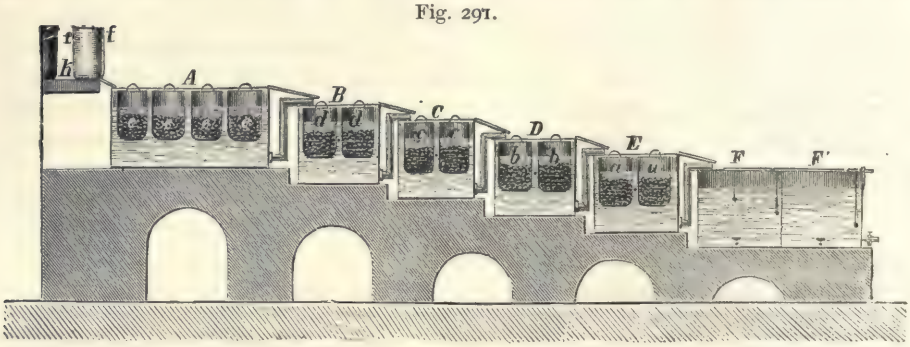
Fig. 290.



The lixiviation apparatus introduced by Clément Desormes (Fig. 291) consists of a number of sheet-iron tanks arranged like steps. The number of the tanks is from twelve to fourteen (the figure gives only five, *A*, *B*, *C*, *D*, *E*). The upper tank, *A*, is of cast iron, and is twice the size of the rest. By means of bent iron pipes, which are fixed about 15 centimètres from the bottom, the liquid of each tank can be let off into the next lower one, from *A* into *B*, from *B* into *C*, and so further. The lowest tank, *E*, delivers the liquid into the settling cisterns, *F F'*, of which there are six, and which are connected with each other by pipes fixed about 10 centimètres below the upper margin.

The crude soda to be lixiviated, finely ground, is placed in sheet iron vessels, *e*, *d*, &c., perforated like sieves. When the lixiviation is to begin the tanks are filled with hot water, two of the sheet-iron vessels, each charged with 50 kilos. of crude soda, are suspended in the lowest tank, *E*, by means of a rod thrust through its handles; after from 25 to 30 minutes they are taken out and transferred to *D*, whilst two fresh ones are placed in *E*, &c., so that in eight hours, if we have a set of 14 lixiviation tanks, there are not only in *A* such soda vessels which have been in all the others, but two, *f*, have been already taken out of *A*, and are placed to drain upon *h*. After thirty minutes the residue from all these vessels is emptied into a truck for removal from the works, whilst *e* is put to drain in the place of *f*, *d* in the place of *e*, &c., and in *E* there are placed two newly filled vessels. Whenever two new vessels are thus placed in the

Fig. 291.



lowest tank there is run into *A* about twice as much water as the volume of the soda. The water pushes out the heavier lye at the bottom, which flows through the connecting-tube into tank *B*, and causes the heavier lye to flow over into *C*, &c., so that at last an almost saturated solution flows from *E* into the cistern *F*, where all turbidities settle. The temperature in the lixiviating tanks must be kept at from 40° to 50°, not higher, as the calcium sulphide might undergo a decomposition. The heat is kept up by means of steam pipes, which open into the tanks at about a third of their height. In the settling cistern also the lye is heated by steam to prevent it from crystallising. The suspension of the soda in perforated vessels in the lixiviation tanks is the well-known method by which substances to be dissolved or lixiviated are placed at the surface of the solvent, so that the more concentrated solution may not accumulate about the bodies to be dissolved and prevent the action of the solvent, but may flow to the bottom and continually make room for the solvent. If the vessels when filled with crude soda are of such a magnitude that they cannot be raised by the workmen, this is effected by means of a set of pulleys.

Fig. 292.

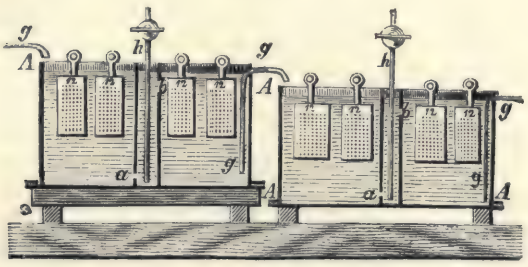
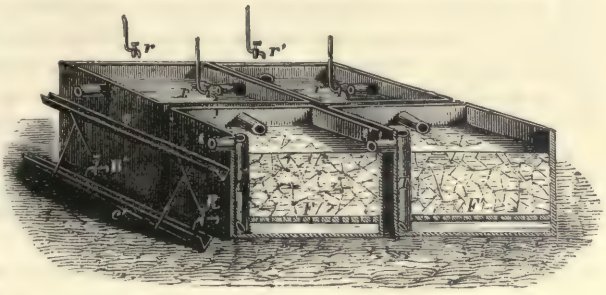


Fig. 292 shows two lixiviation tanks of a modified design. Each tank is divided into two compartments by a double vertical partition, which communicate with each other by the openings, *a* and *b*. Into the space between the two partitions, the steam-pipes, *h*, open; *g* are the overflows; the strainers, *12*, of sheet iron, are provided at their narrow ends with perforated strips that the rods for lifting them may be thrust through.

According to Dürre, four tanks of wrought or cast iron, of about 1·6 metre long, 1·6 broad, and 1·65 in depth, are placed like terraces. In each of these are put 500 kilos. of crude soda, broken into four-inch lumps, with the needful quantity of water. The lixiviation is effected in twelve hours, during which the soda is changed four times, being placed after every three hours in the next higher lixiviating tank, so that in twelve hours the residuum is thrown out from the top tank as exhausted. In the two highest tanks the lixiviation is effected cold, in the third at 44°, and in the fourth at 56°. From the top tank the lye passes straight into the following one, and from that into a cistern, where it is heated by steam. Whilst in the three upper tanks water is added every three hours, from the lowest tank the lye flows off into a larger cistern at the suitable concentration, 38° Tw. Four such series of tanks with their accessory heating vessels form a system.

The so-called Shanks—more correctly Buff-Dunlop—lixiviation apparatus utilises the fact that a solution becomes the heavier the more salts it holds in solution, and that a column of a weak lye may be counterpoised by a shorter column of stronger lye. On this principle the tanks, four to eight in number (Fig. 293), stand side by side horizontally. Water runs through them, and as it passes it lixiviates the soda and becomes denser from tank to tank, from the first, which contains clear water, to the last, from which saturated soda lye runs off. Although the vats stand in a horizontal plane, the level of the liquids forms steps. Each is provided with a false bottom, *F*, of perforated sheet metal. From the bottom of each there passes a tube, *T*, open at both ends, its lower aperture being cut diagonally up to the surface, and supports laterally a short tube, *t*, which, as will be seen from the figure, connects one tube with the next. The main, *r*, fitted with cocks, supplies each tank with water. Four washings suffice as a rule. One tank contains crude soda which has undergone three lixiviations, and therefore only a small quantity of soluble salts. This vat (I.) contains therefore washing water, which after it has taken up everything soluble from the soda enters tank (II.), which has only been lixiviated twice; the lye then passes into tank (III.), the contents of which have only been washed once; and, lastly, into tank (IV.) charged with fresh soda.

Fig. 293.



From here the lye travels to the collecting cistern. Tank (I.) is charged with crude soda, and the track of the lye is modified as required by means of the plugs placed in the apertures of the pipes. This arrangement allows the workman to seek out two contiguous vats, and to take the one as the entrance- and the other as the exit-vat. As the vats are alternately filled and emptied, the one which has been last charged contains the richest mass and the most saturated lye, which is densest, and stands lowest; consequently this vat is the exit-vat for the new series, from which the saturated lye is drawn. On the other hand, the tank in which the mass is most exhausted contains the weakest lye, which has the highest level. This tank serves as the entrance vessel for pure water. As soon the charge in this tank is completely exhausted it is removed and replaced by a new charge; by opening a series of cocks, this tank is made the exit-tank. At the same time the current of

cold water is led into the adjacent vat, &c. The more tanks a series contains the more readily a given quantity of crude soda can be exhausted in a given time. Still there are practical limits which cannot be exceeded, both for the number of the lixiviation tanks and for the rapidity of the stream of water. It is sufficient if the lye running off has a sp. gr. of 1·27–1·286, which answers to a proportion of soda of about 13·5 per cent. of the weight of the liquid.

The advantages of this procedure are: (1) The transfer of the crude soda from vat to vat is done away with, as the charge remains in the same vessel until it is exhausted, which represents a considerable economy in labour. (2) The crude soda is always covered by the liquid, so that it never cakes together, as happened in the old process, to the great hindrance of the lixiviation. (3) The ascending current of the liquid carries off the densest part of the solution, so that the lixiviation is effected with less water, in less time, and also more completely than by a descending filtration. (4) The rapidity and the continuity of the operation remove the alkali quickly from the action of the insoluble calcium sulphide, and abridge the duration of the reactions by which soluble sulphides are formed to the disadvantage of the product. (5) The high concentration of the lye abridges the time of evaporation and thus effects an economy of fuel.

The nature of the lye obtained by the lixiviation of the crude soda and its clarification on standing depends on the quality of the soda, the time of the action of air and water, and the temperature employed. Dry crude soda contains no caustic soda, the presence of which in the lye depends on the action of lime on the sodium carbonate in presence of water. Sodium sulphide occurs only in traces in a normal crude soda, but its quantity in the lye is still more variable than that of caustic soda, and depends on the manner of its lixiviation. It is chiefly monosulphide which is contained in the lye: if a polysulphide is present, it is converted into monosulphide by the action of the caustic soda. The quantity of water used in lixiviation has no influence upon the causticity of the lye, whilst the quantity of sodium sulphide increases with the quantity of water, the duration of the digestion, and the increasing temperature and concentration. This is a consequence of the increased solubility of calcium sulphide, which in contact with water is resolved into calcium hydrosulphate and calcium hydroxide; the former compound yields, with caustic soda, sodium sulphide, and this the more readily the higher the concentration. Sodium carbonate is also decomposed with calcium sulphide, and this the more readily the more dilute the solution, the higher the temperature, and the more prolonged the action. The practical conclusion is that crude soda should be lixiviated rapidly with the smallest quantity of water and at the lowest possible temperature. It would be a great improvement if an apparatus were invented which would lixiviate the soda in a few hours and with so little water as to yield at once a concentrated lye. Such lye would be free from sodium sulphide.

The lyes may contain iron as sulphide, as carbonate, and as sodium ferrocyanide. Iron sulphide occurs in solutions of sodium carbonate only if they contain sodium sulphide. The iron sulphide deposits completely from such solutions on prolonged standing. The deposition is not promoted by the addition of sodium bicarbonate, as is erroneously assumed, but by that of dense iron sulphide, which carries down that in solution, or more probably in fine suspension. Iron occurs as carbonate in solutions which have been freed from sodium sulphide by means of a metallic oxide, *e.g.*, zinc oxide, and have been afterwards treated with carbon dioxide. A solution of sodium carbonate containing bicarbonate dissolves iron oxide in considerable quantity. The solution is quite colourless, and does not deposit iron even on long standing. An addition of caustic soda quickly and completely removes iron from such solutions.

Iron sometimes occurs as ferric acid in melted caustic soda, but only as a result of bad workmanship. Iron sulphide and sodium ferrocyanide are found in crude soda lyes.

As an example of the composition of a crude lye, the analysis of a lye is quoted obtained from the works of Matthes & Weber at Duisburg. Sp. gr. = 1·25. 1 litre lye contained 313·9 grammes solid salts, consisting of—

Sodium carbonate	71·250	per cent.
,, hydrate	24·500	,,
,, chloride	1·850	,,
,, sulphide	0·102	,,
,, thiosulphate	0·369	,,
,, sulphide	0·235	,,
,, cyanide	0·087	,,
Alumina	1·510	,,
Silica	0·186	,,
Iron	traces	

Purification and Concentration of the Lye.—The lye, when freed by settling from all suspended matter, contains chiefly sodium carbonate and caustic soda, besides common salt and small quantities of other sodium salts. The presence of iron-sodium sulphide in the lye is to be noticed, as it is the cause of the colour of soda-ash. To eliminate these disturbing iron-compounds it is necessary to let the lyes remain for some time in the settlers, when the iron sulphide is deposited. For decomposing the ferrocyanide Hurter and Carey heat the lye in a worm to 180°. If a solution of sodium thiosulphate is heated with potassium ferrocyanide in a closed tube there occurs a peculiar decomposition. A greenish-grey precipitate subsides, having the composition $KFeCy_3$. The rest, exactly half the cyanogen, occurs in solution as potassium sulphocyanide. The decomposition takes place according to the following equation :—

$$K_4FeCy_6 + 3Na_2S_2O_3 = KFeCy_3 + 3KCyS + 3Na_2SO_3.$$

But if the solution contains sodium carbonate the ferrocyanogen is completely decomposed, the iron separating out as ferrous oxide according to the equation :

$$Na_4FeCy_6 + 6Na_2S_2O_3 + 2Na_2CO_3 + H_2O = 6NaCyS + 6Na_2SO_3 + 2NaHCO_3 + FeO.$$

Further, a part of the cyanogen is split up into ammonia and formic acid, or sodium formiate, so that the equation which most accurately represents the reaction taking place in the lyes is the following :—

$$Na_4FeCy_6 + 5Na_2S_2O_3 + 2NaCO_3 + 3H_2O =$$
$$5NaCyS + 5Na_2SO_3 + NaCHO_2 + NH_3 + 2NaHCO_3 + FeO.$$

The sulphide can also be removed by oxidation, as it is done in Gossage's process by means of atmospheric air. Pauli promotes the oxidation of the sulphur compounds in the crude soda lye by the addition of a little manganese oxide. Parnell desulphurises by means of zinc or zinc oxide.

The lye is evaporated to a certain degree of concentration, when from the supersaturated and boiling liquid sodium carbonate is separated as a crystalline powder with 1 mol. water : $Na_2CO_3 + H_2O$.

It is fished out in proportion as it separates ; during these operations fresh quantities of lye flow in from the more elevated pans, and this is continued for weeks or months as long as a sufficiently pure salt is obtained. At first the quantity of carbonate in the lye greatly preponderates over the quantity of the other constituents above named, but in time the proportion becomes less favourable. Hence the carbonate as it separates out becomes more and more impure, and is accompanied by common salt, and the mother liquor which adheres to the salt contaminates it more and more. The mother liquor ultimately remaining contains chiefly caustic soda and sodium sulphide, an excess of these reduces the solvent power of the lye for salts almost to *nil*. The soda-salt, fished out and freed as far as possible from the mother liquor by drainage or in a centrifugal machine, is dried on the hearth of a reverberatory fed with coke, with constant stirring, and calcined, in order to oxidise the sodium sulphide of the adhering mother-liquor and obtain a perfectly white product. This product is soda-ash (calcined soda)

The character of this soda-ash and its percentage of carbonate vary greatly. The different sorts known in commerce are obtained by separating the salt into classes according to the length of the evaporation of the lye. That first obtained is the best quality; as the evaporation is prolonged it becomes worse, and it is at the option of the manufacturer how many sorts he will produce. A soda containing 90 per cent. of alkaline matter is said to be one of 90 degrees. The rest is sulphate and common salt with a small quantity of sulphite produced during calcining.

According to K. W. Jurisch, at the works of J. Muspratt, of Widnes, a series of samples of crude soda have been examined—*i.e.*, from a revolver furnace in July 1874 (I), from a hand-furnace in November 1874 (II), from a revolver furnace in April 1876 (III), in the same works, and in February 1876 from a similar furnace in the works of Ch. Tennant at St. Rollox (IV).

	I.	II.	III.	IV.
Na_2CO_3	41·592	41·760	46·154	45·280
NaCl	1·205	1·386	0·673	1·740
Na_2SO_4	1·213	2·264	0·353	1·505
Na_2SO_3	0·145	0·534	—	—
$Na_2S_2O_3$	—	0·315	0·593	1·135
SiO_2	2·375	4·090	2·680	3·120
Al_2O_3	1·080	1·503	0·785	1·021
Fe_2O_3	0·877	1·107	1·015	0·724
$CaCO_3$	11·616	6·636	9·686	5·114
CaO	5·689	5·816	1·695	1·328
CaS	29·783	31·938	33·615	30·985
MgO	—	0·303	0·404	0·295
Coal	4·425	3·260	3·500	7·370

The proportions of the ingredients used were the following:

	I.	II.	III.	IV.
Salt cake	100	100	100	100
Limestone	106	109	78	73
Coal	55	56	47·5	41
Mactear's lime	—	—	7·3	7

During the months of December 1879, January, February, and March, 1880, daily samples were taken of the revolver crude soda-lyes, and the mixture was analysed every week. One litre contained in grammes:

	Mean.	Highest.	Lowest.
Total Na_2O	187·980	198·380	168·950
Na_2O as Na_2CO_3	147·930	161·180	131·750
Na_2O as NaOH	40·050	47·740	37·200
Na_2CO_3	252·910	275·560	225·250
NaOH	51·680	61·600	48·000
NaCl	10·682	15·503	6·274
Na_2SO_4	2·793	3·755	1·944
Na_2SO_3	0·291	0·543	0·150
$Na_2S_2O_3$	1·327	2·080	0·980
Na_2S	4·149	5·043	2·925
Na_4FeCy_6	0·768	1·050	0·510
SiO_2,Al_2O_3,Fe_2O_3	4·656	5·630	3·850

In February there were further taken daily samples of the red liquor (II), of the oxidised red liquor (III), and of the causticised red liquor (IV), and analysed at the end of the month. In comparison with the mean of the February analyses of the revolver crude soda lyes (I), 1 litre contained in grammes:

	I.	II.	III.	IV.
Total Na_2O	191·270	189·630	158·800	116·850
Na_2O as Na_2CO_3	149·270	106·300	81·430	14·440
Na_2O as NaOH	42·010	83·330	77·380	102·410
Na_2CO_3	255·200	181·790	139·220	24·690
NaOH	54·200	107·520	99·840	132·140
NaCl	9·719	26·413	19·481	12·650
Na_2SO_4	2·953	11·809	9·143	7·204
Na_2SO_3	0·306	5·603	1·126	2·396
$Na_2S_2O_3$	1·437	6·085	9·693	2·948
Na_2S	4·188	8·424	1·262	2·507
Na_4FeCy_6	0·710	2·280	1·500	0·280
SiO_2, Al_2O_3, Fe_2O_3	5·118	6·700	4·610	0·960
Specific Gravity	1·279	1·290	1·235	1·170

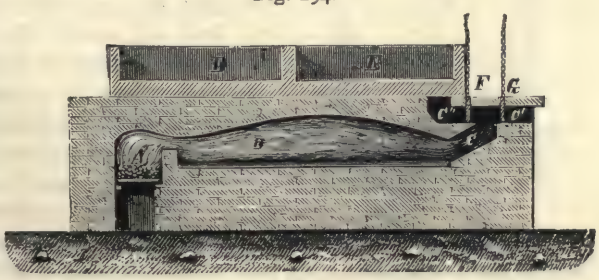
The red liquor dropping from the revolver salts (II.) is slightly diluted by condensed steam, with which the salts are treated for their better purification. The oxidation of the red liquor was effected by forcing in air with a Körting blast, with the joint use of Weldon mud; the causticising took place, according to Parnell, at a pressure of 3 atmospheres. The analyses confirm the opinion that almost all the impurities of the crude soda-lye pass into the red liquor, so that on oxidation its sodium sulphide is converted into sodium dithionate, and on causticising according to Parnell's process the latter is partially reconverted into sodium sulphide and sulphite. The lime also precipitates silica, alumina, and iron oxide, apparently also some cyanogen.

Jurisch further gives the mean (II.), the highest (III.), and the lowest (IV.) values from twenty daily analyses, September 1879, of revolver soda (made by Pechiney's process) by the Runcorn Soap and Alkali Company, referred to 100 parts total soda present as Na_2CO_3 and NaOH, and for comparison the analysis of a sixteen days' average sample of crude soda-lyes from hand furnaces (Muspratt's works), March 1880 (V.), as also the mean of the January analyses of the revolver. Crude soda-lyes all are given in column (I.):

	I.	II.	III.	IV.	V.
Na_2O as NaOH	21·290	13·320	15·160	8·500	33·570
NaCl	5·930	—	—	—	7·279
Na_2SO_4	1·720	4·142	5·400	2·800	6·042
Na_2SO_3	0·164	—	—	—	0·383
$Na_2S_2O_3$	0·666	1·486	1·630	1·200	1·081
Na_2S	2·053	1·433	1·820	0·930	1·359
Na_4FeCy_6	0·358	0·216	0·348	0·174	0·150
SiO_2, Al_2O_3, Fe_2O_3	2·373	—	—	—	2·730

If the crude soda-lye is at once evaporated to dryness, so that no mother liquor remains, the reverberatory (Fig. 294) is used. A thick layer of the soda-salt is first rammed down upon the sole of the furnace to prevent the lye from coming in contact with the bricks. As soon as the furnace has been raised to dull redness by the coke fire burning in *A*, the lye, which has been concentrated to 55° Tw., is let flow down from the heating pans, *D* and *E*, into the furnace. As soon as it touches the hot soda-salt a violent boiling begins; the mass rises and falls and is easily brought to dryness. The salt is kept in powder by stirring with iron rabbles. As soon as a sufficient

Fig. 294.



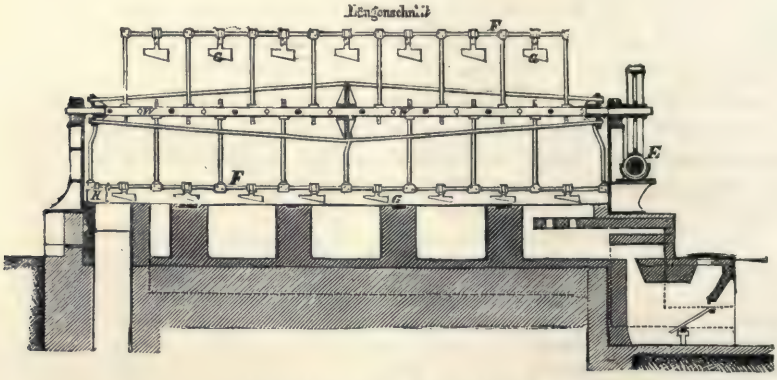
quantity of salt has been obtained the further flow of the lye is stopped, and the dry salt is drawn out of the furnace. The gases of combustion can be led either into the chimney or underneath the lye-pans, *D* and *E*, through the traps, *F* and *G*, and the flues, *C*, *C'*.

J. Brown, on analysing the soda ash, obtained by concentrating the crude lye:

	I.		II.
Sodium carbonate	68·907	...	65·513
,, hydroxide	14·433	...	16·072
,, sulphite	7·018	...	7·812
,, thiosulphate	2·231	...	2·134
,, sulphide	1·314	...	1·542
,, chloride	3·972	...	3·862
,, aluminate	1·016	...	1·232
,, silicate	1·030	...	0·800
Insoluble matter	0·814	...	0·974
	100·000	...	100·000

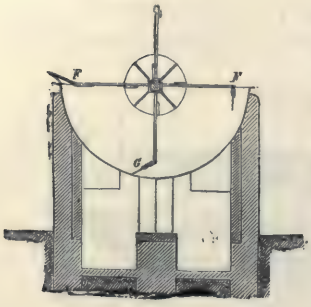
If a reverberatory fire is used, a part of the sulphur dioxide contained in the smoke-gases is absorbed by the soda-lye, so that the soda is reduced in value. At the

Fig. 295.



Längenschnitt—Longitudinal Section.

Fig. 296.



Rhenania works and at Saarau, according to the suggestion of Thelen, the evaporation of the soda-lyes is conducted in a hemispherical pan of 1 metre radius and 7 metres in depth. In the shaft, *W*, moved by the helix, *E* (Figs. 295 and 296), rods, *F*, are fixed, carrying shovels, *G*, fixed obliquely. On passing through the lye, they touch the bottom of the pan, push the salt on towards the end, where it is removed by a shovel to be dried in similar drying apparatus.

For producing soda crystals,* $Na_2CO_3 + 10H_2O$ (with 63 per cent. of water), the soda-ash is dissolved in hot water, clarified by standing, and the liquid is let cool in large iron vessels, when it deposits large crystals. The soda-salt is often dissolved in pans of sheet-iron (Fig. 297), into which a current of steam is passed through the pipe, *C*. The soda to be dissolved is placed on the sieve-like perforated sheet-iron vessel, *D*,

* Sal-soda of American writers.

which can be raised or lowered. The pan is filled through the pipe, *C*, to three-quarters its depth with water, and the vessel, *D*, containing the soda, is next introduced, whilst steam is blown in through *C*. As soon as the lye shows a sp. gr. of 50° to 53° Tw. it is run into the sheet-iron crystallisers, which are about 5 metres long, 2 broad, and 0·45 metre deep, and which should be placed in a cool, airy place At a medium temperature, the formation of the crystals is complete in about five to six days. After the mother liquor has been let off through an aperture at the bottom of the crystallising vessels it is then worked up to a low-grade soda: * the crystals are removed from the sides and submitted to re-crystallisation.

For this purpose, the soda-crystals are dissolved in a conical sheet-iron pan, *A* (Fig. 298), which is directly heated by the flame of the fire, *C*. By means of the flues, *D*, the flame plays quite round the pan. The pan is filled with crystals, a little water is introduced through *B*, and heat is applied. The crystalline water is sufficient to melt the salt. The fire is then withdrawn, the pan is covered with a wooden lid, and the liquid is let settle. When it has become clear, the lye is conveyed by syphons into a cistern, and thence into quadrangular cisterns of sheet-iron of 40 to 50 centimetres in diameter. Here the crystallisation begins, and is completed in about eight days. After the mother liquor has been removed from the crystals, the iron vessels are set

Fig. 297.

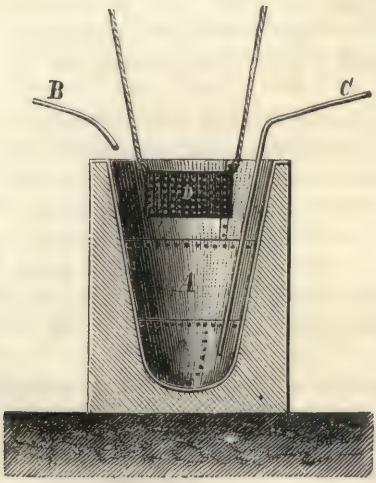
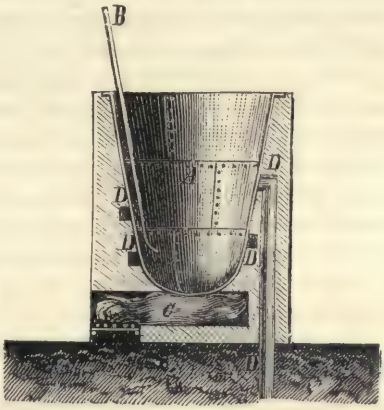


Fig. 298.



for a short time in a pan of boiling water, when the crystals are detached from the wall in consequence of beginning to melt, so that on merely inverting the vessels the crystalline mass falls out in a body. After draining, the mass is broken up, dried in a desiccating chamber at 15° to 18°, or at once packed in casks to prevent and efflorescence.

The crystalline state affords a guarantee for purity (supposing that the crystals were not produced from a mixture of sodium carbonate and sulphate, in which case they may contain large proportions of sulphate—sometimes up to 50 per cent.). The more general employment of soda-crystals is prevented by their high proportion of water, which increases the freight.

Melting pans for soda must be constructed of a different kind of iron pan from salt-cake pans. Resistance to acids demands a large proportion of carbon in chemical combination; whilst resistance to alkalies requires, on the other hand, a high percentage of graphite and a low percentage of combined carbon. In the former case,

* So-called "weak ash."

the iron must contain much manganese and little silicon, but in the second case much silicon and as little manganese as possible. From one and the same mixture of irons we may obtain either only good salt-cake pans and bad soda-pans, or bad salt-cake pans and good soda-pans; or, what most frequently happens, medium salt-cake pans and medium soda-pans. Melting alkalies dissolve the combined carbon with a deep-brown colour, manganese as a manganate, and phosphorus as a phosphate, so that iron is mostly attacked when these substances are present in quantity. Graphite, silicon, and ferrosilicon are very slowly attacked by alkalies. In order to determine the resistence to alkalies of a sample of cast iron, 5·6 grammes of it are heated to quiet fusion with 6·2 grammes caustic soda; the melt is dissolved in water, and the loss in weight of the iron is determined. For determining the resistance to acids, the sample should be laid in melting acid potassium sulphate; 5·6 grammes of a salt-cake pan on fusion with 27·2 potassium bisulphate should lose at most 25 per cent.

Theory of the Formation of Soda.—It was formerly assumed, according to the explanation of Dumas, that, on calcining a mixture of sulphate, limestone, and coal, the coal, producing carbon monoxide, reduced the sulphate to sodium sulphide, which was then decomposed, with the formation of sodium carbonate and calcium oxysulphide and the escape of a part of the carbon dioxide.* According to the view of Unger, which essentially agrees with that of E. Kopp (1865), after the sodium sulphide has been formed, the calcium carbonate loses carbonic acid, and there remains behind a mixture of caustic lime, sodium sulphate, and carbon, which is transformed into caustic soda and calcium oxysulphide: the soda takes up carbon dioxide, and is converted into sodium carbonate.

The latter view probably approaches nearest the truth; but it is not necessary to assume the existence of a calcium oxysulphide in order to explain the inaction of calcium sulphide with sodium carbonate, since calcium sulphide is almost insoluble in water (1 part calcium sulphide requires 12,500 parts water at 12·6° for solution). The excess of lime employed in practice, doubtless favourable for the purity of the product, is sufficiently explained by the circumstance that the lime, as an infusible solid, does not come into full action in the soda-melt, which, though a soft paste, is by no means a liquid. The excess of lime is to be regarded merely as representing the coarser particles which remain inactive.

During the formation of soda in the furnace the existing carbon becomes carbon dioxide—

$$5Na_2SO_4 + 10C = 5Na_2S + 10CO_2; \text{ and}$$
$$5Na_2S + 7CaCO_3 = 5Na_2CO_3 + 5CaS + 2CaO + 2CO_2.$$

However, as during the operation of the formation of soda, and especially towards the end, carbon monoxide is evolved out of the melting mixture and burns with a blue flame, a gaseous development which persists after the melt has been drawn out of the furnace; this carbon monoxide, though it is a secondary product, must be considered in the equation. The formation of carbon monoxide is of great importance, because its appearance shows when the heat is sufficiently high and the mean reaction is at an end. The researches of Unger place it beyond doubt that in the reduction of sulphate by coal there is a formation of carbon dioxide but not of carbon monoxide. This latter gas, therefore, is not formed during the reduction of the sulphate, but is a result of the action of coal upon the excess of chalk or limestone. The reduction of calcium carbonate by coal does not occur until a far higher temperature is reached than that which effects the reduction of the sulphate; it follows upon the latter, *i.e.*, the conclusion of the main reaction. In this stage the sodium carbonate is already formed.

* (α) $Na_2SO_4 + 4C = Na_2S + 4CO$; ($\beta$) $2Na_2S + 3CaCO_3 = 2Na_2CO_3 + CaO,2CaS + CO_2$.

We have therefore to distinguish three stages in the production of soda: at first there is reduction of the sulphate with evolution of carbon dioxide—

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

Then follows the double decomposition between the sodium sulphide just produced and the calcium carbonate: $Na_2S + CaCO_3 = Na_2CO_3 + CaS$; then occurs a partial reduction of the excess of calcium carbonate employed by the carbon ($2CaCO_3 + 2C = 2CaO + 4CO$).

On lixiviation the caustic lime occasions the formation of caustic soda.

Theory consequently requires only 20 parts of coal to 100 parts sulphate. The customary addition of carbon in excess (40 to 75 per cent.) is advantageous from a two-fold point of view: first, as a substitute for that which has reduced a part of the carbon dioxide to carbon monoxide; secondly, the addition renders it possible to seize the exact moment when the reaction is completed and the melt must be withdrawn from the heat of the furnace, *i.e.*, after the liberation of carbon monoxide has begun and before it has ceased.

Utilisation of the Leblanc Soda-Residues.—As already pointed out, the Leblanc process has furnished (until quite recently) the chief quantity of the soda, caustic soda, and bicarbonate which are consumed. This superiority over all other processes is due in great part to the production of the soda-residues, in as far as they have the property of being easily and completely separated by lixiviation from the alkali contained in the crude soda. At the same time, these residues form the darkest side of this important branch of chemical industry. The great quantity of sulphur which enters into this process is lost in the residues in such a manner that at the alkali-works of Dieuze, in Lorraine, the sulphur stored up in the solid residues, down to the year 1869, was estimated at the value of 43 million marks, or in round numbers £2,300,000. Each ton of alkali yields 1½ ton of dry residues, and the masses produced in this manner are generally piled up in heaps near the works, forming hills of considerable elevation. These residues, especially in warm weather, evolve sulphuretted hydrogen in serious quantity, which annoys and injures the inhabitants of the district. Moreover, the rain and the surface waters which come in contact with these heaps extract from them a more or less intensely coloured liquid containing calcium sulphide and polysulphide, which poisons the wells and water-courses into which it penetrates. All attempts to recover this sulphur in a simple and cheap manner, and thus to do away with the nuisance and the danger to the public, have until recently proved fruitless.

The soda-residues (tank-waste or vat-waste) from the "Silesia" works at Saarau have, when dry, according to E. Richters (1869), the following composition:

Calcium sulphide	37·62	38·04	39·10 (= 16 to 18 % S)	
Iron sulphide	1·88	1·75	2·01	
Calcium thiosulphate	2·69	3·02	2·35	
„ carbonate	23·18	22·24	24·02	
„ sulphate	1·68	1·01	1·38	
„ sulphite	0·74	0·31	0·63	
Lime (CaO)	6·49	7·00	7·25	
Alumina	2·11	2·02	2·00	
Soda	2·52	2·10	1·86	
Silica (combined)	4·24	4·03	4·62	
Water	2·32	3·29	1·51	
Sand	7·74	6·82	7·21	
Carbon	5·41	6·00	6·39	
Magnesia	0·64	0·51	0·70	
	99·26	98·17	101·06	

Chance gives the following analysis, executed in June 1882 :—

Works	Gaskell, Deacon & Co., Widnes.	British Alkali Co., Widnes.	Netham Chemical Co., Bristol.	Radcliffe Chemical Co., Manchester.	Jas. Muspratt & Sons, Widnes.	Jarrow Chemical Co., South Shields.	C. Tennant & Co., St. Rollox, Glasgow.	J. C. Gamble & Sons, St. Helens.	Chance Brothers, Oldbury, near Birmingham.	
	Revolver.	Revolver.	Revolver.	Revolver.	Hand.	Revolver.	Revolver.	Hand.	Hand.	
Soda mixture—										
Salt cake	100·00	100·00	100·00	100·00	—	100·00	—	100·00	100·00	100·00
Limestone	86·00	86·00	95·0	105·00	—	100·00	—	105·00	105·00	105·00
Coal	40to42	40·00	53·0	33·33	—	57·00	—	57·50	65·00	65·00
Sulphur—										
Total in waste	26·33	24·29	23·52	22.66	20·73	17·94	18·84	19·47	17·22	18·04
Recoverable	25·28	23·87	23·10	21·30	19·87	17·83	17·59	17·17	15·59	16·83
Per cent.	96·02	98·27	98·21	94·00	95·85	99·39	93·36	88·19	90.53	93·29
Soda residues—										
Sodium carbonate	3·16	2·57	—	0·45	—	—	—	3·69	1·63	1·97
Sodium oxide	—	—	1·47	—	—	—	1·17			
Sodium hydrate	—	—	—	—	—	1·88				
Calcium carbonate	21·19	28·10	20·07	38·14	35·26	27·92	28·41	23·64	38·81	36·92
Calcium hydrate	trace	—	5·92	7·62	—	8·60	4·90	8·89	9.53	8·85
Calcium sulphide	56·89	53·77	52·03	47·97	44·75	40·16	39·62	38·67	35·12	37·90
Calcium thiosulphate	1·07	—	—	—	—	—	1·19	2·85	1·49	0·68
Calcium sulphite	trace									
Calcium sulphate	trace	—	trace	—	3·76	—	2·13	0·91	—	0·20
Calcium silicate	3·53	1·47	—	—	—	2·96	—	4·19		
Carbon	7·20	9·62	13·69	0·30	5·72	12·33	8·03	5·86	6·27	7·04
Magnesium carbonate	—	—	—	—	—	—	1·35	0·98		
Magnesium oxide	—	—	0·16	—	0·42	2·13	—	—	—	trace
Alumina	1·02	0·74	1·98	—	2·45	2·13	8·62	1·01	0·13	0·34
Ferric sulphide	1·65	1·16	1·16	3·74	—	0·29	0·70	2·16	2·76	2·44
Ferric oxide	—	—	—	—	1·64					
Silica	—	—	1·50	—	—	—	—	—	1·21	1.34
Sand	2·82	0·89	2·09	2·51	6·00	0·66	3·98	7·41	2·61	1·79
Total	98·53	98·32	100·51	100·73	100·00	99·06	100·10	100·56	99·56	99·47
Moisture in fresh water	29·20	29·41	27·50	—	—	—	—	—	30·40	29·96

It was not until 1863 that soda was regularly obtained from vat-waste, *i.e.*, by the process of Guckelberger (improved by L. Mond), of Schaffner (of Aussig), of P. W. Hofmann (of Dieuze), and of Schaffner and Helbig (1878). The earlier processes depend on the conversion of the insoluble calcium sulphides in the waste into soluble compounds by means of oxidation effected by atmospheric oxygen, lixiviation of the oxidised mass, and precipitation of the sulphur present in the lyes (in the form of polysulphides and of thiosulphate) by the addition of an acid, hydrochloric acid being always used as a matter of course in actual practice.

The earliest process of Schaffner consists of the following operations: the production of the sulphur-lye, its decomposition, and the precipitation of the sulphur.

For obtaining the sulphur-lye, the vat-waste is subjected to an oxidation process in the air by being thrown up in heaps. The heaps heat in time, and the formation of polysulphides, and on further oxidation that of thiosulphates, begins. Practice soon teaches how long a heap should lie. After some weeks the heap has a yellowish-green colour within, and is ready for lixiviation. It is broken up and remains for twenty-four hours exposed to the air, when the oxidation is complete. The lixiviation is effected with cold water, as in the case of crude soda; so that at the conclusion only concentrated lyes come into play. After this lixiviation process the waste is once more oxidised by placing it in pits 1 metre in depth and width, made near the lixiviation tanks. This oxidation

in pits is more rapid than the former oxidation. The former lixiviation process has made the mass more porous, so that the air has better access, and there are formed more thiosulphates along with the polysulphides. Or, instead of putting the residues in these pits, they can be let remain in the lixiviation tanks, and the second oxidation can be accelerated by forcing the gases from a chimney under the double bottom of the lixiviation-tanks. Labour is thus economised, as the filling and emptying the pits is dispensed with. This kind of oxidation is very energetic, and in eight to ten hours the mass is again ripe for lixiviation. This oxidation may be repeated from three to ten times, according to the character of the waste. The furnace gases decompose the calcium sulphide in such a manner that polysulphide and thiosulphate are formed. The gases must not be employed too hot. The lyes from the first oxidation consist chiefly of polysulphides and thiosulphates : in those of the second lixiviation the thiosulphate predominates, and in the third this is still more the case. All the lyes are mixed in a common tank. The product of this operation is therefore a lye of calcium polysulphides with a certain proportion of thiosulphates.

The decomposition of the lye with hydrochloric acid is effected in closed apparatus of cast-iron or stone. In the decomposition of calcium thiosulphate by hydrochloric acid, sulphurous acid is evolved and sulphur separates out:

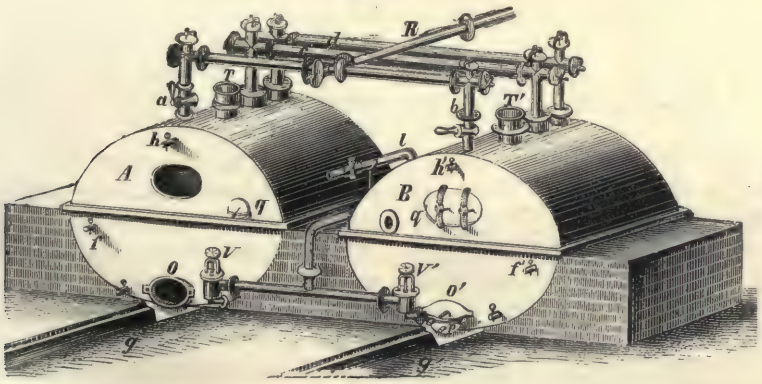
$$CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S + H_2O.$$

The sulphurous acid further decomposes the polysulphide into calcium thiosulphate with elimination of sulphur:

$$2CaSx + 3SO_2 = 2CaS_2O_3 + Sx.$$

By titration the sulphur-lye may be tested for its proportion of polysulphide and thiosulphate, and the waste may be oxidised accordingly. Fig. 299 shows the cast-iron precipitating apparatus as generally introduced. *A* and *B* contain the lye to be

Fig. 299.



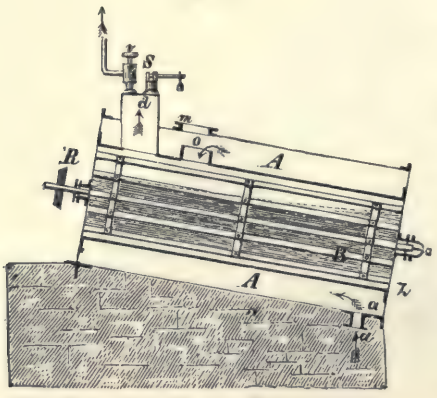
decomposed. By means of a flexible tube attached to *l*, the lye is directed either through *q* into *A*, or through *q'* into *B*. Earthen pipes, *T*, serve for introducing the hydrochloric acid. The tubes, *c* and *d*, likewise correspond with the gas apparatus; *c* is placed on the cover of *A*, whilst its long limb opens into the liquid in *B*; at *d* we have the reverse case—the short limb is on the cover of *B*, whilst its long limb plunges into the liquid in *A*. The cock *a* is closed when the gases have to pass through *c* into the liquid in *B*; the cock *b* is closed if the gases have to pass through *d* into the liquid in *A*. Any superfluous gas escapes through *R*. After the decomposition steam is blown in through the valves, *V* and *V'*, in order to expel any residue of sulphurous acid absorbed by the liquid. When the process is at an end, the sulphur flows out, with the chloride of calcium lye, through the aperture, *O*. At first the wooden plug is opened, and the

chief part of the calcium chloride lye is allowed to flow out. In order to find whether all the sulphurous acid is expelled, the cock *h* is opened, and the escape of sulphurous acid, if occurring, is detected by the smell. The cocks *f f'*, serve to show whether the apparatus is properly filled with lye, and to judge of the progress of the decomposition. The sulphur obtained is finely granular and contains a little gypsum ; it flows with the calcium chloride liquor in a channel, *g*, and from here into a cistern with a double bottom ; the lye flows off and the sulphur is left behind ; it is washed with water, and then undergoes the melting or purifying process.

The sulphur from the precipitating apparatus is placed in a closed cast-iron pan with so much water that the mass has a pasty composition, and steam is let enter at the pressure of $1\frac{3}{4}$ atmosphere. In this manner the sulphur melts under water, the calcium chloride lye adhering to it is taken up by the water, and the gypsum becomes distributed as a fine crystalline powder. The fused sulphur collects at the lowest part of the pan, and can be run off and cast in moulds. When all the sulphur is removed the gypserous water is let flow off, and sulphur and water are sharply separated from each other by their specific gravities. Along with the sulphur a small quantity of lime is put in the pan to take up any free acid. The excess of lime forms, on melting, calcium sulphide, and if the sulphur is arseniferous the arsenic sulphide dissolves in the calcium sulphide and passes into the supernatant water. On melting under water it is not necessary to carefully wash and dry the sulphur : distillation is dispensed with, and the sulphur is freed from arsenic by one and the same process. The method of smelting with steam pressure has the advantage that the sulphur is only heated enough to become a thin liquid and cannot be overheated, which is important as regards the subsequent casting.

Fig. 300 shows the melting-pan. A cast-iron cylinder, *B*, lies in a wrought-iron cylinder, *A*, the ends of both being screwed together. The apparatus slopes to one end, so that the melted sulphur may collect at the lowest part. Into the inner cylinder are put the sulphur, and the needful quantity of water, and there is in this cylinder a shaft with arms turned by means of the toothed wheel, *F*. The sulphur is introduced at *m*. The steam enters at *a* into the wrought-iron cylinder, surrounding the cast-iron cylinder *B*, into which it enters at *o*, and after the fusion is complete it is let escape from the dome, *d*, provided with a safety-valve, *S*. The melted sulphur is let off at *z*. In this manner from 50 to 60 per cent. of the sulphur present in the waste is obtained in the state of pure sulphur. To 1 part sulphur there are used 2 to $2\frac{1}{2}$ per cent. hydrochloric acid.

Fig. 300.



Mond's Recovery Process.—Guckelberger observed that, by oxidising and lixiviating the vat-wastes, solutions are obtained which contain not merely thiosulphate, but polysulphides in quantity, and which, with acids, give a precipitate of sulphur. Like Schaffner, Guckelberger also found that the waste after being once lixiviated yielded further quantities of lye on repeated oxidation and lixiviation. The experiments were carried on for Guckelberger by L. Mond, who afterwards continued them on his own account, and arrived at the following process :—

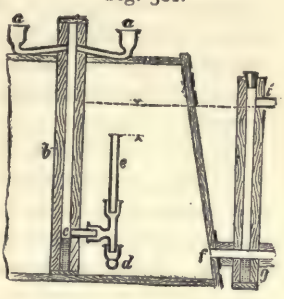
The waste remains in the lixiviating vats, the number of which is increased threefold. The space between the two bottoms is connected by a tube to a blast, the work

of which can be regulated by a slide in the tube. As soon as the last lye has been drawn off air is blown in. The waste is heated by reason of the accelerated oxidation up to 94°; watery vapours escape, and on the surface of the mass there appear white shining spots. From the quantity of the vapours, the number of the spots, and the temperature, it is seen whether the suitable degree of oxidation has been reached. The waste is then covered with water and submitted to a methodical lixiviation. The liquids obtained in the successive lixiviations are collected and conveyed to the precipitating apparatus. The precipitation of the sulphur is effected by means of hydrochloric acid in a wooden vessel closed with a cover, in which is a stirring apparatus, an escape-pipe for gases, and an inlet pipe for steam. Hydrochloric acid and sulphur-lye are admitted alternately. The decomposition ensues without any escape of sulphuretted hydrogen or sulphurous acid, if certain proportions are observed which have been ascertained by practice. According to Mond, this is the case when the equivalents of the thiosulphates in the sulphur-lye are to those of the polysulphides as 1 : 2. He assumes that the decomposition of these compounds of hydrochloric acid is effected almost exclusively according to the following equation—

$$CaS_2O_3 + 2CaSx + 6HCl = 3CaCl_2 + 3H_2O + xS.$$

The temperature of the liquid in the precipitating apparatus should not fall below 40° nor exceed 60°. In the former case the precipitated sulphur does not deposit completely, and in the latter there are formed large quantities of gypsum, which mix with the sulphur. The decomposed neutralised lyes are drawn off into settling cisterns. The sulphur collecting at the bottom was formerly washed, dried, and at once melted.

Fig. 301.



Schäppi gives here the following working directions:— The longer the lye and the oxidised residue are left in contact the more sulphide is dissolved, and the more strongly the mass may be oxidised without danger of having it over-blown. It is best to oxidise as strongly as possible, and to lixiviate as long as possible (two to three hours). The weaker the lye, the richer it is in sulphides; the stronger, the richer it becomes in hyposulphite. The more we oxidise, therefore, the weaker the solution must be kept. Schäppi generally works with a solution of 16° Tw. (hot). When he began to work with a solution of 12° Tw. (hot) he could oxidise with a double quantity of air without obtaining an over-blown lye, thus obtaining a better yield of sulphur. With hot water, not only far more sulphide is dissolved in a short time, but, what is more important, the residue is not cooled. Hence the residue after the lye is drawn off oxidises at once well, whilst, otherwise, four to six hours are required before it becomes again sufficiently hot for energetic oxidation. If it is decomposed on the large scale, so that lye and acid mix, with exclusion of air, before entering the decomposer, there is a twofold gain: the loss of sulphuretted hydrogen by imperfect decomposition is unimportant and the decomposer works better. One precaution must be observed: the lye must be kept at between 80° and 90° by means of waste steam, as the sulphur otherwise does not admit of filtration.

From the decomposer the solution flows through the pipe, *f* (Fig. 301), upon the filters directly at *g*, and at *i* circuitously. Within the decomposer a perforated beam, *b*, is placed laterally, and is connected by the aperture, *c*, with the ascending stoneware pipe, *e*. The lye and the acid flow together (with a hydraulic joint) through the two bent stone-ware pipes, *a*, mix on the way to *e*, and discharge into the upper layer of the decomposer, and flow off to the filters, after being completely worked through by the mechanical agitator below in the decomposer. The stone-ware pipe, *d*, bent at right angles, opens into a channel in the wall of the decomposer. In general it is closed

with a plug, or with a flexible tube, or a pinch-cock. On setting the decomposer to work, half the contents are run out, *d* is then opened in order to empty the pipes *b* and *c*, so that they may not be stopped by the deposit of sulphur.

For every residue there is a certain specific gravity to which the sulphur lyes must be brought, and which depends on the time of oxidation, the time of lixiviation, and the volume of air used for oxidation. The longer we oxidise, and the more air we use, the weaker the lye must be kept; the longer and hotter we lixiviate, the stronger the lye must be, in order to obtain the most advantageous composition. The attempt must be made with very strong oxidation to keep the specific gravity of the lye so low that it is a little over-blown.

At St. Salindres, air is blown into the yellow lye of the vat-waste by means of a Körting blast up to the point where on treatment with acid neither H_2S nor SO_2 is given off, and the decomposition with hydrochloric acid then follows. Much may be here economised, because during the operation of oxidation about one-fourth of the lime, in passing from CaS to CaO, is deposited in a very dense condition, and can be easily filtered off, whilst sulphides are formed richer in sulphur.

Recovery of Sulphur by P. W. Hofmann.—At the works at Dieuze a process was developed between 1864 and 1866 which, in addition to the recovery of the sulphur from vat-waste, aimed at reviving the manganese from the waste of the chlorine stills. The vat-waste had been piled up for more than thirty years. Close to the works flows a streamlet, which afterwards touches the town of Dieuze. This stream takes up all the sulphur compounds flowing from the waste in rainy weather, as well as the acid manganese liquors. The water, for a distance of 6 to 8 kilometres, was coloured black by the precipitate of iron sulphide, and contaminated the air with hydrogen sulphide to such an extent that the authorities threatened to close the works unless the nuisance was promptly removed.

The experiments made by P. W. Hofmann led finally to the following results:—As in the other procedures for the recovery of sulphur, soluble sulphur compounds are first produced by the oxidation of the waste. This oxidation is effected in heaps, which are previously mixed with iron sulphide precipitated from the neutralised manganese liquors. Experiments proved that the addition of iron sulphide promoted the oxidation. The waste, after six or seven days' exposure to the action of the air, was lixiviated, yielding a liquid which was known as *eaux jaunes sulfurées*. The residues were oxidised twice more and treated with water, the second and third oxidation not requiring more than three days each. The solution thus obtained contains principally calcium thiosulphate, and was called *eaux jaunes oxydées*. The united liquids from the lixiviations were let flow into a tank made of stone flags, made water-tight at the junctions with asphalt, and let mix with the acid manganese, which had been previously clarified by twenty-four hours' rest in a similar tank. The decomposition of the sulphur-lye is effected at the expense of the free acid existing in the manganese chloride, as well as of the free chlorine and the ferric chloride. The separation of sulphur begins at once, without the escape of hydrogen sulphide, if the respective proportions of the two "yellow waters" were correct. In order to prevent any such escape the sulphur-lye is led, not at once into the cistern, but into a conical apparatus of sheet-iron. It is provided at half height with two openings, through which pass two tubes, extending down to within a few centimetres of the bottom of the cone. A little higher there are two other openings, through which the liquid can flow off into the cistern. The manganese liquor and the sulphur-lye are let flow in simultaneously through the two tubes, and in such quantity that the efflux openings are kept constantly closed by the inflowing solutions. The first reaction takes place within the cone; any H_2S formed collects in its upper part, and is led off through a pipe issuing from the apex of the cone, at the end of which it is burnt. The sulphurous acid formed is carried off by a tube

into a vat filled to two-thirds of its height with *eaux jaunes sulfurées* and kept in constant motion by a mechanical agitator. The SO_2 converts the calcium polysulphides of the *eaux jaunes sulphurées* into calcium thiosulphate, whilst sulphur is separated. The thiosulphate is decomposed with sodium sulphate and used for preparing sodium thiosulphate.

The sulphur collecting on the false bottom of the sulphur vessel is washed and dried. The neutral manganese liquors are pumped into underground tanks with puddled clay bottoms, and with sides of bank waste piled up on woodwork. As soon as the liquid is clear, it is drawn into other recipients, in which the last traces of suspended matter quickly settle. The residual mass of iron sulphide is intimately mixed with the vat-waste produced daily, and exposed in heaps to the oxidising action of the air, as already described. The neutral manganese liquors, freed from iron and clarified, are mixed in a special receiver with the yellow sulphur-lye, producing a deposit which contains all the manganese along with a quantity of free sulphur. This precipitate is let settle, the supernatant liquor (calcium chloride) run off upon linen filters, washed with water, and the residual mass dried upon stone flags.

The dried manganese consists of a mixture of manganic oxide and free sulphur. In order to utilise the latter, the mixture is roasted and the SO_2 is passed into the chambers. The residue consists of mangano-manganic oxide, with 40 to 45 per cent. of manganese sulphate. The latter is dissolved out with water, yielding a mass which consists of pure mangano-manganic oxide, free from iron, and hence fit for use in the glass manufacture, where iron gives a green colour. From the aqueous solution manganese sulphate may easily be obtained by evaporation. It is then mixed with sodium nitrate, and the mixture is heated in the sulphur furnaces with formation of sodium sulphate and manganese nitrate, the latter of which is at once resolved into higher oxides of manganese and hyponitric acid. The hyponitric acid passes into the chambers along with the sulphurous acid, and aids in the conversion of the latter into sulphuric acid. If the ignited mass is lixiviated with water, sodium sulphate dissolves and manganese oxides remain, containing about 55 per cent. of manganese peroxide, and capable of being used in the production of chloride of lime. From the solution of sodium sulphate, Glauber's salts may be obtained by crystallisation, and it is used for the decomposition of the neutral solution of calcium chloride. There is obtained, especially on stirring, a gypsum of fine texture, which may be used in place of china clay in the paper manufacture.

The more or less profitable application of one or the other process for recovery depends much on the nature of the vat-waste, on the cost of labour, and on the price of sulphur or pyrites. Muddy waste cannot be advantageously oxidised in Mond's process, and oxidation in heaps is here to be preferred. Hofmann's process is somewhat complicated, but the results are said to be satisfactory.*

The precipitation of sulphur by the processes of Mond and Guckelberger is effected most completely when free sulphurous acid is present in the lye, mixed with hydrochloric acid exactly in such a proportion that in the fresh lye all the sulpho and hydrosulpho compounds are converted into thiosulphates. The thiosulphates, if the process works normally, are exactly converted by a fresh quantity of hydrochloric acid into sulphurous acid and free sulphur, the former of which serves exclusively for converting the sulphides into thiosulphate. As the liquid which runs off must be neutral, a small quantity of sulphur is always lost in it in the form of dissolved thiosulphate.

According to Divers, when moist vat-waste is exposed to the air there takes place, first, hydration of the calcium sulphide. The most important of the hydrogenised compounds are: calcium hydrosulphide, a colourless crystalline salt, which in the air is quickly decomposed to form calcium hydrate and calcium hydroxyhydrosulphide.

* Probably labour is cheap there. It does not appear to have been widely adopted.

This latter compound, CaSH.OH.3Aq., is deposited from a solution of calcium hydrosulphide which has been mixed with lime and sugar. The compound is likewise produced if solid calcium hydrate is placed in a solution of calcium hydrosulphate, and if calcium hydrate is treated with sulphuretted hydrogen. In solution the compound is quickly decomposed with separation of calcium hydrate. In a concentrated solution of calcium hydrosulphate the compound is insoluble and is then not decomposed by water. The calcium sulphide in vat-waste passes first into calcium hydroxyhydrosulphide, and this is the source of calcium hydrosulphate. As the former compound is insoluble with solution of calcium hydrosulphate, only weak solutions are obtained in lixiviating vat-waste. Concentrated lyes of hydrosulphate easily give off hydrogen sulphide and form calcium hydroxyhydrosulphide. The two latter facts have hitherto frustrated all attempts to dissolve out the bulk of the sulphur in vat-waste in an inexpensive manner.

Divers believes that the best process for extracting the sulphur from vat-waste in the form of hydrogen sulphide is to treat it successively with steam in about four vessels. By gradually oxidising and lixiviating the vat-waste, we obtain a mixture of calcium polysulphide and thiosulphate. A formation of bisulphide was formerly assumed, but now it is found that the products are tetra- and penta-sulphide. Hydration of calcium sulphide precedes all other changes:

$$CaS + H_2O = Ca.SH.OH. \qquad Ca.SH.OH + H_2O = CaO_2H_2 + H_2S.$$

$$Ca.SH.OH + H_2S = CaS_2H_2 + H_2O.$$

Wet vat-waste laid in covered heaps contains, in addition to unaltered calcium sulphide, calcium hydroxyhydrosulphide, calcium hydrate, and free sulphuretted hydrogen. Oxygen during the oxidation of vat-waste acts upon the free sulphuretted hydrogen which is constantly being formed. As has long been known, H_2S is readily, though slowly, oxidised. The experiments of Divers show that the direct oxidation of calcium hydrosulphate by air is extremely tedious. He therefore concludes that only the free hydrogen sulphide, and not its calcium compounds in vat-waste, is oxidised by the air. Sulphur, if boiled with lime, yields calcium pentasulphide and thiosulphate:

$$3CaO_2H_2 + 12S = CaS_2O_3 + 2Ca_2S_5 + 3H_2O.$$

It must be assumed that when the reaction takes place at a boil with ready-formed sulphur it will also take place in the cold with nascent sulphur from the oxidation of vat-waste. The chemistry of the oxidation of vat-waste is thus much simplified. The fixed products of the hydrolysis of calcium sulphide are calcium hydrate and hydrogen sulphide; the latter is oxidised by the air to free sulphur, whilst pentasulphide and thiosulphate are formed with the hydrate of lime.

Whilst in the process depending on the oxidation of calcium sulphide only half the sulphur is recovered, the lime and the remaining half of the sulphur forming a vat-waste of the second order, Schaffner and Helbig recover all the lime and all the sulphur in a useful form. Their process for producing sulphur from vat-waste and sulphurous acid with the simultaneous recovery of the earths combined with sulphur as carbonates depends on the use of magnesium chloride for decomposing the calcium sulphide according to the formula:

$$CaS + MgCl_2 = MgS + CaCl_2, \text{ and } MgS + 2H_2O = Mg(OH)_2 + H_2S.$$

The calcium carbonate is not decomposed by the magnesium chloride. The magnesium chloride employed is recovered as vat-waste residue; it consists of the magnesia, the calcium chloride, and the other ingredients which did not enter into reaction after the expulsion of the hydrogen sulphide. This is exposed to the action of CO_2, when calcium carbonate and magnesium chloride are formed according to the formula:

$$MgO + CaCl_2 + CO_2 = MgCl_2 + CaCO_3.$$

Instead of using magnesium chloride alone, a portion of it may be taken, hydrochloric acid being alternately or simultaneously introduced, when the liberated

magnesia is dissolved and exerts its action again. Sulphuretted hydrogen is converted by sulphur dioxide into sulphur, according to the formula: $2H_2S + SO_2 = 3S + 2H_2O$.

There are here formed, however, not merely sulphur and water, but tetrathionic and pentathionic acid, &c. This injurious bye-reaction is greatly lessened (though not prevented, as the inventors assume) by the use of solutions of calcium and magnesium chlorides. If there is an excess of one or other of the gases, this has no effect upon the reaction. It is not yet decided what is the part taken by these chlorides in the reaction, but it is certain that one equivalent of calcium or magnesium chloride is required for the total sulphur present. The decomposition of the vat-waste with magnesium chloride is effected in heat in large closed iron vessels, fitted with agitators. Either the vat-waste is gradually introduced into the total quantity of magnesium chloride required to fill the generator, or the magnesium chloride is let flow into the entire quantity of vat-waste, or both substances are simultaneously introduced into the vessel in equivalent proportions. The escape of sulphuretted hydrogen is thus prevented so that no pressure can arise in the generators and decomposers; further in the sulphuretted hydrogen decomposers a larger quantity of SO_2 is always kept in store than corresponds to the H_2S flowing in from the generators. The silica and alumina in the vat-waste, which, if they remained in the recovered lime, would soon accumulate, so as to render it useless, are removed by elutriation or by passing the residues of decomposition through a fine sieve. The recovery of the magnesium chloride and the lime from the residues thus freed from slags (silica and alumina) is effected by passing into them air containing carbon dioxide (combustion gases). According to Chance, the hydrogen sulphide burns to sulphur dioxide.

According to a recent proposal of Schaffner, the magnesia may be used for decomposing the sal-ammoniac lyes of the ammonia soda works.

According to C. Opl, the sulphur is to be dissolved as calcium hydrosulphate by treating vat-waste with sulphuretted hydrogen. The process is being introduced in the Rhenania works, as recently, in consequence of a rise in the price of hydrochloric acid, the recovery of sulphur on Mond's process has become unprofitable.

Of particular importance is the new process of Chance, which carries out the reaction: $H_2S + O = H_2O + S$. The hydrogen sulphide and other gases, chiefly nitrogen, are allowed to mix with an accurately regulated quantity of air in the proportion of $H_2S + O$. The gases are burnt beneath the grate of a circular shaft tired with fire-stones. Upon the grate there lies first a layer of brick, and then one of ferric oxide. The latter is heated to dull redness by the reaction itself, and in this state it effects the almost completely smooth combustion of hydrogen sulphide to watery vapour and sulphur vapour. The vapours produced pass first into a small brick chamber and thence into a large chamber. The former soon becomes so hot that the subliming sulphur melts and can be drawn off in this state. But very much sulphur passes in the form of vapour into the large brick chamber, flowers of sulphur condensing at the front and water at the back. As the escaping gases still contain a small quantity of unchanged hydrogen sulphide and also of sulphur dioxide, they are passed through suitable purifiers before escaping into the air.

As the success of this process depends in the first place on the exact equivalence of the quantity of oxygen to that of the hydrogen sulphide—but the percentage of the latter fluctuates greatly in consequence of the use of impure carbonic acid—it is important to obtain the latter of rich and uniform composition. This is effected by utilising the experience obtained in the ammonia-soda process, according to which lime-kiln gases are obtained containing 30 per cent. of carbonic acid. But even with this, in all earlier experiments for decomposing vat-waste, gaseous mixtures were obtained containing very variable quantities of hydrogen sulphide, and, of course, with a very large admixture of foreign gases. Chance has succeeded in greatly reducing these

mixtures and in producing a fairly constant yield, so that he can now obtain with certainty at pleasure either sulphurous acid or sulphur. He makes use of the long-known reaction, that carbonic acid acts upon calcium sulphide in the presence of water, so that there is at first a production of calcium hydrosulphate—

$$2CaS + CO_2 + H_2O = CaCO_3 + Ca(SH)_2.$$

An excess of carbonic acid decomposes the hydrosulphate and expels all the sulphuretted hydrogen: $Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S$.

In the practical execution of the process the vat-waste is made up with water to a thin paste, which is passed through a sieve to remove all coarse parts, and in this state is conveyed into tall cylinders, into which the gases of the lime-kiln are pumped. A battery of seven cylinders, 4½ metres high and 1·8 metre in diameter, is sufficient to treat the residue from the weekly working of 300 tons salt-cake. In the first vessel the CO_2 saturates the free lime and then drives out the H_2S, according to the above equations. The latter, being driven into other vessels, encounters fresh vat-waste and is there absorbed with the formation of calcium hydrosulphate: $CaS + H_2S = Ca(SH)_2$, so that for a time the escaping gases contain mere traces of CO_2 and H_2S and consequently may escape into the air, though for safety's sake they are passed through lime or iron-oxide purifiers. In this manner considerable quantities of useless gases are got rid of. In time the sulphuretted hydrogen appears in more than traces. This is detected when in one of the intermediate vessels the gas which escapes on opening a cock can be ignited. The course of the gases is then changed; the passage from the last receiver into the air is closed and a pipe leading to a gas-holder is opened. Into this the gases are passed as long as they are sufficiently rich in H_2S. When this ceases the pipe is shut off, and as in the meantime the vat-waste in the first cylinders is fully desulphurised, it is taken out and replaced by a fresh charge, so that the process begins again; the cylinders which were first coming in turn last. The introduction of carbon dioxide is continued until the clear filtrate from the cylinders no longer gives a reaction with a salt of lead. The residue now consists chiefly of calcium carbonate in the form of mud, but containing 2·5 to 3 per cent. of soda in the form of bicarbonate, which is utilised when this mass is used in the decomposition furnace. Another useful application is that for cement, and in both respects this residue is better than that of the Schaffner-Helbig, process as the following analyses show:—

	Lime Residue.—Schaffner-Helbig.				Lime Residue.—Chance.		
Calcium carbonate	75·62	79·32	76·48	71·14	84·79	87·16	86·32
„ sulphate	4·60	3·89	4·62	4·52	0·36	0·49	0·36
„ chloride	0.36	0·25	0·30	1·51			
„ silicate	—	—	—	—	1·91	2·30	2·35
Magnesium carbonate	0·60	1·77	0·70	—	1·34	1·03	1·07
Magnesia	2·50	1·67	2·85	3·20			
Magnesium chloride	0·88	0·78	1·70	2·58			
Sodium carbonate	—	—	—	—	0·45	0·55	0·63
„ sulphate	—	—	—	—	0·07	0·21	0·07
„ silicate	—	—	—	—	1·47	1·42	1·00
Alumina	0·96	0·80	0·76	0·94	1·19	1·47	1·35
FeS	—	—	—	—	1·05	0·71	0·99
Fe_2O_3	2·30	2·60	1·34	1·07			
Coke	5·80	3·72	3·00	3·80	4·06	2·06	2·98
Sand	—	—	—	—	0·97	0·56	0·85
Silica	0·50	0·30	1·12	3·45			
Sulphur	—	—	—	—	0·45	0·54	0·40
Moisture (to 100°)	4·65	4·30	6·00	6·00	0·58	0·39	0·34
Water and loss					1·31	1·11	1·29
Combined silica	—	—	—	—	1·71	1·89	1·72
SO_3	—	—	—	—	0·25	0·41	0·25
S, as sulphide	—	—	—	—	0·38	0·26	0·36
S, free	—	—	—	—	0·45	0·55	0·40
Soda, soluble	0·95	0·85	0·70	1·75	0·26	0·32	0·37
Soda, insoluble					0·75	0·72	0·51

The water running off from this process is clean enough to flow into any stream; it is best utilised for making up fresh waste into a paste. It contains grammes per litre:

Alkalinity, as $NaHCO_3$, calculated as Na_2O	6·63	to	8·61
Alkaline earths calculated as $CaCO_3$	1·50	„	2·16
Total sulphur	0·22	„	1·11
Sulphur as sulphates	traces	„	0·01
„ as thiosulphates	0·05	„	0·23
„ as sulphides	—	„	0·00
Silica	0·00	„	0·08
Alumina, ferric oxide		traces	

The sulphuretted hydrogen is collected in a gasometer of 15 metres diameter and 4·2 metres effective height, containing 850 cubic metres. The water-joint is completely shut off from the air by a layer of coal-tar oil boiling at a very high temperature. The composition of the gases varied, in eight analyses made in four days, only from 32·3 to 34·0 H_2S and 1·10 to 2·0 CO_2 (using lime-kiln gases of 27·0 to 29·1 per cent. CO_2).

The gas burns at once if lighted. The heat is sufficient to work the Glover tower, and to concentrate acid set in lead pans on or around the furnace. The chamber room is the same as the pyrites furnaces, and the consumption of nitre ranges from 1·15 to 1·44 per cent. on the acid produced, calculated as SO_3.

In working for several months a complete set of chambers in this manner, 90 per cent. of the sulphur found analytically in the vat-waste had been recovered; 8 per cent. were lost as iron sulphide, as SO_2 and H_2S in the main separation, in consequence of accidental leakages, &c.; 5 per cent. remained in the coarser parts sifted out, which will be utilised by improved arrangements.

Of the H_2S taken from the gasometer, 98 to 99 per cent. were recovered as sulphuric acid. The acid is perfectly free from arsenic, contains a mere trace of iron, and is nearly colourless. From November 1877 to March 3, 1888, more than 3000 tons of vat-waste were worked up, and about 40 tons SO_3 were produced weekly.

The expense of the process is very small. The outlay for the installation is only one-half of that for the Schaffner-Helbig process. The cost of labour for the entire process is smaller than that for breaking up pyrites, serving the pyrites furnaces, and carrying off the burnt ores. No fuel is required, except that for raising the steam used in pumping the lime-kiln gases. An alkali manufacturer who makes either caustic alkali or chloride of lime requires for each of these operations more quicklime than that corresponding to the quantity of kiln-gases required for treating the vat-waste. Brock (of the firm of Sullivan & Co.) estimates the total cost of the sulphur at 1*d.* per unit—*i.e.*, about 8*s.* 6*d.* per 21 cwt. or 1067 kilos.

The economy of Chance's process can best be appreciated if we realise that at present 300,000 tons of pyrites are used annually in England in the Leblanc process, and that their sulphur has till lately passed into the unendurable mounds of vat-waste. If, in future, as Chance hopes, the pyrites sulphur may be obtained gratis from the mining companies, and if the vat-waste were worked upon the Chance process, there would be obtained in England yearly 300,000 tons of sulphur, of which 30,000 to 40,000 would be used in this country, and the rest would be available for exportation. It is to be remarked that, in 1887, 312,446 tons were exported from Sicily, of which 88,593 tons went to America.

The Ammonia-soda Process.—If ammonium bicarbonate in a concentrated solution is brought in contact with saturated brine, or preferably if the brine is mixed with finely powdered ammonium bicarbonate, the less soluble sodium bicarbonate separates as a crystalline powder, and the supernatant liquid is a watery solution of ammonium chloride: $2NaCl + 2NH_4.H.CO_3 = 2NaHCO_3 + 2NH_4Cl$.

As sodium bicarbonate passes into sodium carbonate at dull redness:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2,$$

we have here the foundation of a process for the manufacture of soda, where, of course, the ammonia required for precipitating fresh quantities of common salt must be recovered by means of lime or magnesia:

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

Dyar and Hemming carried out the industrial production of soda from common salt and ammonium bicarbonate in England as early as 1838. The next process, of Schloesing and Rolland, for which they took out a British patent in 1855, contained certain improvements, but it was essentially similar to the process above described. Schloesing used for the manufacture strong brine, which was saturated with ammonia and carbon dioxide. Ammonia and carbonic acid were let act upon the brine; the separation of the precipitated bicarbonate from the liquid was effected by means of a centrifugal machine. If the soda is to be perfectly pure, the salt is washed in the centrifugal machine with a solution of bicarbonate. The calcination of the bicarbonate and the consequent conversion into soda are effected in a cylinder of sheet-iron. The carbon dioxide is collected as it escapes. The manufactory of Schloesing and Rolland, at Puteaux, near Paris, ran from 1855 to 1857, and yielded 25 tons of ammonia soda monthly.

After the ammonia-soda process had been attempted with more or less success by Gerstenhoefer of Freiberg, Honigmann of Aachen, and many others, E. Solvay of Brussels introduced it in his works at Couillet in Belgium, and subsequently at Varangéville-Dombasle, near Nancy.

The conversion of sodium chloride into bicarbonate is effected in three connected pieces of apparatus, the first serving to prepare the concentrated brine, the second for saturating the solution with ammonia, and the third for decomposing the ammoniacal liquid by means of carbon dioxide. The apparatus in which the brine is saturated with ammonia is a cistern of tin-plate, or of wood lined with lead, taller than it is wide. It has a perforated false bottom, beneath which the ammoniacal gas enters, which is divided by the holes into many separate bubbles, and is easily absorbed by the brine. The liquid increases considerably in volume, whilst its density falls from 37·6° Tw. to 18° to 21° Tw. As considerable heat is liberated on the absorption of the ammonia, the saturated solution is first passed into a vessel, where it is cooled by a stream of cold water flowing in a worm, and then into the absorber, in which it is decomposed by carbonic acid. This gas may be produced in any convenient manner.

As an absorber there is used a cylinder as shown in section in Fig. 302. In this cylinder, *a*, lie a number of finely perforated plates, *b*, of the shape of the segment of a globe. Fig. 303 is such a plate seen from above. In *a* there are also a number of plates, *c*, with one hole or a few holes, which give passage to the gas and the saturated solution, without allowing the freshly entering liquid to mix with that at the bottom, which is nearly saturated. In the margin of the perforated plates there are teeth, *z*, cut out so that the liquid and the gas may pass through when the apertures are partly choked. The absorber is always kept nearly full of liquid whilst carbon dioxide is forced in from below through the pipe *d*. By this means the gas is not only kept in very intimate contact with a liquid moving in the opposite direction, but it also exerts, in consequence of its expansion, a considerable mechanical power, and consumes thereby such a quantity of heat that the heating of the liquid is prevented (as would otherwise be the case on the absorption of carbonic acid by the ammonia), and which could not be otherwise easily avoided. The liquid enters through a pipe, *e*, at about half the height of the cylinder, into which it flows out of a trough, so that its level is kept uniform, about 3 metres from the upper end of the cylinder. The trough is closed, and is connected with the upper end of the cylinder by a tube, which maintains an equal pressure in both. One trough can supply several absorbers. In this manner the liquid is reserved only in the upper half; it sinks down very slowly, and is soon saturated

with carbonic acid suited for taking up all the ammoniacal gas which the gas may bring with it from the lower part of the absorber. The absorbers must be so high that at least half the carbonic acid entering from below is absorbed, and, at the same time, all the ammonia contained in the liquid may be converted into bicarbonate. A height of 11 to 16 metres, when the gas must be forced in at a pressure of $1\frac{1}{2}$ to 2 atmospheres, gives the best results. It is well not to let the gas enter in an uninterrupted current, as an irregular motion prevents the bicarbonate separated out from attaching itself to any one place. The liquid saturated with carbonic acid is best allowed to run out in portions every three minutes; the suspended bicarbonate is collected in a vacuum filter and washed in a very small quantity of water. In a cylinder, *g* (Figs. 304 and 305), there are at suitable distances from each other a number of round plates, *h*, with openings at the centre and at the circumference. A shaft, *i*, passes through the cover in the bottom of the cylinder and carries arms, *k*, with scraping knives, *l*, which push the mass lying on the plates alternately towards the circumference of one plate and towards the middle of the following, so that it gradually passes from the top plate to the bottom of the cylinder. The plates are hollow, and can be heated by the introduction of steam or hot gases of any origin from the pipe *m*. The bicarbonate is introduced by means of an apparatus, *n*, which resembles the body of a grinding-mill, with arms, *o*, which move slowly. It is always kept full, so that the carbonic acid may not escape here. The dried mass arrives at the bottom of the cylinder in a finely ground state, fit for packing. The gases expelled on drying escape by a tube, *r*, in the cover. If hollow plates are not used the hot gas may be passed directly through the cylinder.

Fig. 306. Fig. 304.

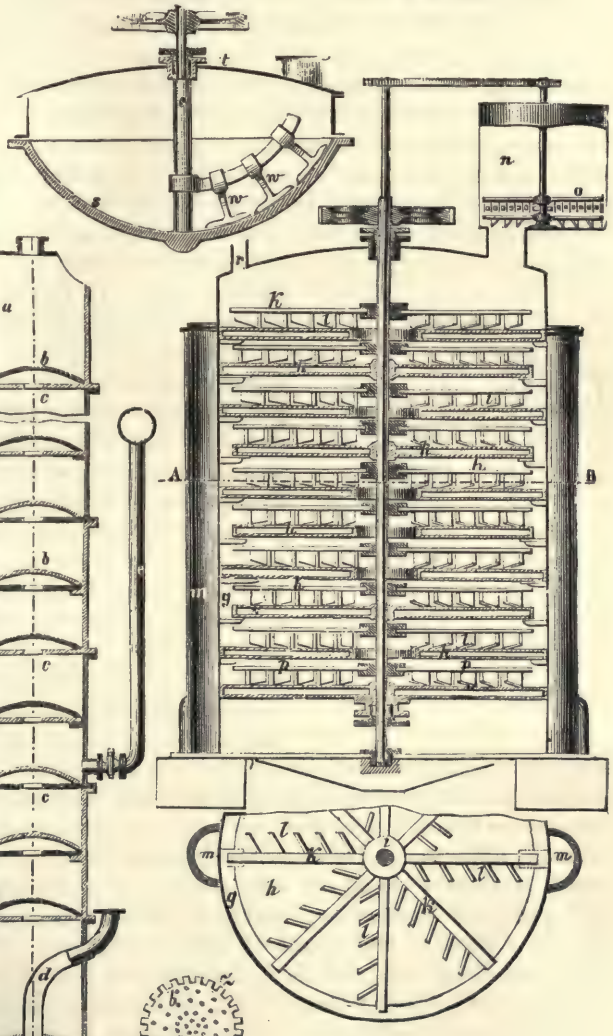


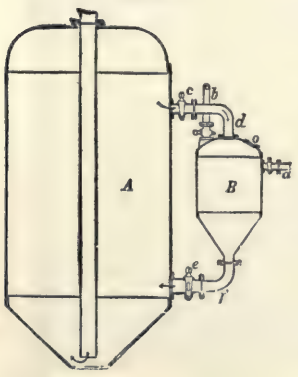
Fig. 302. Fig. 303. Fig. 305.

Another drying apparatus suitable for the production of soda consists of an iron pan, *s* (Fig. 306), closed with a cover, through which passes a vertical shaft in a stuffing-box. The shaft carries arms with scrapers, which stir up the bicarbonate introduced, whilst the pan is raised to a suitable temperature by the fire placed below.

The gas expelled in both these apparatus is carried by an air-pump into a washing apparatus, in which all the ammonia is retained. If soda has been made, the carbonic acid expelled is returned to the absorbers. From the ammonium chloride ammonia is regenerated by lime.

According to H. Schreib, in the present way of working not more than 60 per cent. of the sodium chloride used is converted into bicarbonate. The ammonia present in excess in the ammoniacal lime on saturation with carbonic acid does not, after its conversion into ammonium bicarbonate, enter into the desired reaction with the sodium chloride, but subsides as ammonium bicarbonate. To effect a better utilisation both of the salt and of the apparatus, sodium chloride in a solid form is introduced into the ammoniacal brine used in the ammonia-soda process, during its saturation with carbonic acid in the carbonisation apparatus. In proportion as sodium bicarbonate is deposited, sodium chloride is dissolved, and this is converted into sodium bicarbonate by the ammonium bicarbonate formed in the solution, richer in salts by the continuous passage of the carbonic acid. In this manner it is said that about 80 per cent. of the salt is converted into sodium bicarbonate.

Fig. 307.



For introducing the salt the pan, *A*, containing the ammoniacal brine (Fig. 307) is connected with the brine pan, *B*, by the pipes *d* and *b*. If solid salt is to be introduced the cock *c* is closed and air is forced in through the pipe *a*, so that all liquid is forced out of the pan, *B*. If the cock *e* is also closed we may, after the compressed air has been let out through the pipe *b*, introduce solid salt into *B* through the man-hole, *o*. The man-hole is then closed, and the connection of *A* and *B* is re-established by opening the cocks. The passage of the air containing carbonic acid promotes the circulation both in *A* and *B*. The sodium bicarbonate thus obtained is separated from the liquid in the ordinary manner and converted into soda, whilst the filtrate, which chiefly contains ammonium and sodium chloride (if solid salt is present), is saturated with ammonium carbonate up to 20 to 25 per cent. Sodium chloride passes into solution and ammonium chloride separates out. The reaction is assisted by agitation and strong cooling. After the end of the action the solid sal-ammoniac is filtered out. The filtrate, which contains 20 to 25 per cent. ammonium carbonate, 24 per cent. sodium chloride, and 9 per cent. ammonium chloride, is treated with carbon dioxide in the apparatus, *A*, and returns to the circuit of the manufacture. There is then again formation of sodium bicarbonate and the above-mentioned lye of sodium chloride and ammonium chloride, which is anew treated with common salt and ammonium carbonate. From the sal-ammonium obtained, ammonium carbonate is prepared by treatment with ground calcium carbonate, and as such it is introduced into the apparatus, *A*.

Weldon attempts to combine the ammonia-soda and the Leblanc process by saturating a saturated solution of salt-cake with ammonia and then with carbonic acid, whilst solid salt-cake is further added.

According to G. Carey and F. Hurter, for the same purpose a saturated solution of salt-cake at 50° to 60° is freed from iron, lime, and free sulphuric acid by a certain quantity of soda. The filtered solution is let cool down to 38° and treated with ammonia, 24 to 25 parts of which come to 100 parts of salt-cake. The temperature of

the solution must never fall below 32°, as otherwise sodium sulphate crystallises out; and never rise above 38°, as otherwise the pressure required for completing the reaction would be inconveniently high. So much carbonic acid is then introduced that ammonium carbonate is formed. It is convenient to pass in carbonic acid as soon as the liquid is ammoniacal, as sodium sulphate is more soluble in solutions of ammonium carbonate than in ammonia. As soon as ammonium monocarbonate is formed, it is necessary, in order to complete the reaction, to introduce carbonic acid under pressure. When sodium bicarbonate separates out the solution is let cool. The bicarbonate is washed and freed from the mother liquor by pressure. From the residual solution, which contains ammonium sulphate and carbonate and sodium sulphate, the ammonia is recovered by suitable means.

Whether the proposal of the Croix Company to use trimethylamine instead of ammonia in the production of alkaline carbonates can be used to advantage appears doubtful.

Hasenclever (1880) gives a comparative table of the cost of the two processes, which shows a balance in favour of the ammonia method to which must be added on both sides repairs, lighting, salaries, general expenses, &c. If we disregard the bye-products, ammonia soda is cheaper than Leblanc soda, and the first cost of the installation and the outlay for repairs are lower. On the other hand, the Leblanc process gives a greater scope in sales, if sulphuric acid and salt-cake happen to be in better demand than soda, or if chloride of lime and sulphur are more marketable than hydrochloric acid; whilst the ammonia-soda process does not furnish any intermediate products. Most German establishments work with rock-salt; if cheap brine is accessible, the ammonia soda is in a better position, except the price of fuel at the spot in question if too high.

Cryolite Soda.—Soda is obtained from cryolite, which is opened up by heating with lime—

$$Na_6Al_2F_{12} + 6CaO = 6CaF_2 + Na_6Al_2O_6.$$

The latter compound is soluble in water when alumina is deposited, and is utilised in the state of alum; whilst soda remains in solution. In 1867 five German alkali works consumed 7500 tons cryolite, and produced from it 5500 tons of soda-ash. The Pennsylvania Salt-manufacturing Company consumes yearly in its works at Natrona, near Pittsburg (1876), 1800 tons of cryolite. More and more accessible sources of cryolite are greatly to be desired.

Soda from Sodium Sulphide.—If moist carbonic acid is passed over sodium sulphide (obtained by igniting salt-cake with ground coke), sodium carbonate is formed with the liberation of H_2S—

$$Na_2S + CO_2 + H_2O = H_2S + Na_2CO_3.$$

The process is not likely to survive.

Caustic Soda.—Since the year 1851 caustic soda has become an article of commerce, either as a very strong lye or more frequently as fused hydrate (caustic soda), and it is manufactured on a large scale. It is often still prepared by treating dilute solutions of crude soda (black-ash) with caustic lime: $Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$. The calcium carbonate formed in quantity in this process is mixed with gypsum, and serves for the production of writing- or marking-chalk. In order to economise the fuel for evaporating such dilute solutions the process of Dale is sometimes imitated, who used the dilute lye to feed his steam-boilers and thus brought it up to sp. gr. 1·24 to 1·25. The lye is then further concentrated in cast-iron pans up to sp. gr. 1·9, at which strength it solidifies on cooling.

G. Lunge sought to determine the limits of the conversion of sodium carbonate into sodium hydroxide by treatment with lime. At the common atmospheric pressure the experiments gave the following numbers:—

Per cent. Na_2CO_3.	Before causticising. Specific Gravity.	After causticising in the state of NaOH per 100 parts Soda. I.	II.
2 ...	1·022 at 15° ...	99·4 parts ...	99·3 parts
5 ...	1·052 „ ...	99·0 „ ...	99·2 „
10 ...	1·107 „ ...	97·2 „ ...	97·4 „
12 ...	1·127 „ ...	96·8 „ ...	96·2 „
14 ...	1·150 „ ...	94·5 „ ...	95·4 „
16 ...	1·169 at 30° ...	93·7 „ ...	94·0 „
20 ...	1·215 „ ...	90·7 „ ...	91·0 „

Corresponding experiments, conducted under pressure at 148° to 153°, gave—

Per cent. Na_2CO_3.	Before causticising. Specific Gravity.	After causticising there are out of 100 parts Soda as NaOH. I.	II.
10 ...	1·107 at 15° ...	97·06 parts ...	97·5 parts
12 ...	1·127 „ ...	96·35 „ ...	96·8 „
14 ...	1·150 „ ...	95·6 „ ...	96·6 „
16 ...	1·169 at 30° ...	95·4 „ ...	94·8 „
20 ...	1·215 „ ...	91·66 „ ...	91·61 „

Hence the application of high pressures in causticising offers no perceptible advantage. A more thorough agitation than now commonly takes place is to be recommended.

The use of lime for converting soda into caustic has been abandoned in many establishments, and caustic soda is at once produced in the process of manufacture. This is effected by somewhat increasing the quantity of coal added to the mixture of salt-cake and limestone, and lixiviating the ball-soda at once with water at 50°. After the lye has been let settle it is quickly concentrated to sp. gr. 1·5, when sodium carbonate, sulphate, and chloride sink to the bottom, and the liquid takes a brick-red colour (red liquor), derived from a peculiar compound of sodium and iron sulphides. The lye is then heated in large cast-iron pans, and from 3 to 4 kilos. of soda-saltpetre are added for every 100 kilos. of caustic soda to be produced. As the water escapes, the soda-saltpetre reacts upon the sodium sulphide and the sodium cyanide, which is always present, and there is a plentiful evolution of ammonia and nitrogen. A part of this ammonia is due to the decomposition of the cyanides, whilst another and larger portion is a consequence of the oxidation of the sulphides, when water is decomposed, and the hydrogen reduces the nitric acid to ammonia. When the evaporated mass reaches dull redness, finely divided graphite is seen on its surface.

For the oxidation of sulphides in the production of caustic soda G. Lunge gives the following advice, based upon comprehensive experiments. All sodium sulphide is first oxidised to thiosulphate by atmospheric oxygen. Even if this process were not less costly than nitre, it would be preferable, as the iron of the vessels would be less attacked. Thiosulphate is oxydised by the air only at high temperatures, and slowly, since it is first split up into sodium sulphide and sodium sulphite. The oxidation is therefore hastened by adding nitre. It is useless to do this at temperatures at which the thiosulphate has not been decomposed; the practical rule would be to begin the addition of nitre as soon as, on further raising the temperature, a reaction for Na_2S appears, and then to add gradually small quantities, thus preventing the nitre from coming in direct contact with the iron, and preventing waste of the former and injury to the latter. This method seems to present other advantages. The addition of nitre must cease as soon as neither sodium sulphide nor thiosulphite is present, which occurs at about 300° to 360°. In this manner we reach the most favourable result—the formation of ammonia as the main reaction. Theoretically it would be the more advantageous, as the ammonia might be recovered—a result which should not be pronounced *à priori* impossible; but there is little immediate prospect of an economical solution of the problem. We have, then, all the sulphur as sulphite, or a little of it as sulphate;

by fishing out the salts, a part of the sulphite can be removed along with the sulphate; the main bulk, however, must be oxidised during fusion, preferably not by nitre, which would chiefly be decomposed into nitrogen, but by forcing in a current of air.

The following analyses are obtained from some works in which ball-soda lye, previously desulphurised by means of air, is agitated during causticising by means of a current of air. I. is desulphurised crude lye; crystallises at 20·5°; becomes clear at 24°; sp. gr. at 24°, 1·302; boils at 120°. II. Lye I. diluted and causticised; liquid clear, except a small residue of iron oxide; sp. gr. at 20°, 1·1338; boiling-point, 110°. III. Lye II., concentrated to 45°, before the addition of nitre; clear, except an unimportant grey residue; sp. gr. at 20°, 1·301; boiling-point, 120°. IV. Lye III., evaporated after the addition of nitre, and clarified, ready for the melting-pan; sp. gr. at 18·5°, 1·5417; boiling-point, 150°. V. Salt fished out during evaporation of III.; greyish-white, uniform, soluble in water; all but 0·1 per cent. of residue (chiefly ferric oxide) soluble. VI. Salt deposited on standing from IV. in settling cistern. About a quarter of the whole was removed as a liquid; there remained a dirty mass, which was mixed up.

	Causticised with a Current of Air.					
	I. Crude Lye.	II. Caustic Lye.	III. Evaporated before adding Nitre.	IV. Melting Lye.	V. Fishing Salts.	VI. Clarifying Salts.
	Grammes per Litre.				Grammes per Kilo.	
NaOH	52·0	102·5	267·1	751·6	261·1	283·9
Na_2CO_3	295·4	32·9	77·2	34·1	365·6	241·1
Na_2S	0	0	0	0	0	0
$Na_2S_2O_3$	5·7	2·9	7·1	10·6	5·6	6·0
Na_2SO_3	—	—	—	5·6	4·1	71·1
Na_2SO_4	4·5	2·5	6·7	2·5	38·9	92·1
NaCl	3·1	1·4	3·6	10·6	5·2	4·4
$NaNO_2$	—	—	—	4·7	0	0
Insoluble	—	—	—	—	1·0	6·2
Na_4FeCy_6	trace	trace	trace	—	0	0
Water	941·3	991·6	939·3	722·0	318·5	295·2
Total	1302·0	1133·8	1301·0	1541·7	1000·0	1000·0

Deacon and Hurter for decomposing sodium sulphide pass a weak electric current through the lye. The sulphur is deposited at the anode, which is kept clean by brushing; at the kathode there is formed a corresponding quantity of sodium hydrate. Stronger currents (30 to 50 amp. per square metre of electro) convert the sulphide at once into sulphate. To avoid polarisation they use alternating currents or movable electrodes.

Caustic soda produced in England (1875) contained—

	So-called 60 per cent.		70 per cent.
Sodium hydrate	75·246	...	89·600
„ carbonate	2·536	...	2·481
„ chloride	17·400	...	3·919
„ sulphate	4·398	...	3·419
„ sulphite	0·027	...	0·025
„ silicate	0·297	...	0·304
„ aluminate	trace	...	trace
	99·904		99·748

Caustic soda has its chief uses in the soap manufacture, in obtaining and purifying the products of the dry distillation of lignite, peat, &c., for the purpose of obtaining paraffine, solar oil, and phenol; for purifying petroleum, for preparing soluble sodium

silicate (soluble glass); and of late in considerable quantities in the production of wood-cellulose of alizarine, resorcine, &c.

The subjoined table shows the actual caustic soda contained in lyes of different specific gravities at 15° :—

Specific Gravity.	Baumé.	Twaddell.	Per cent. Na_2O.	Per cent. NaOH.	1 cubic metre contains kilos.	
					Na_2O.	NaOH.
1·007	1	1·4	0·47	0·61	4	6
1·029	4	5·8	2·10	2·71	22	28
1·045	6	9·0	3·10	4·00	32	42
1·060	8	12·0	4·10	5·29	43	56
1·075	10	15·0	5·08	6·55	55	70
1·091	12	18·2	6·20	8·00	68	87
1·108	14	21·6	7·30	9·42	81	104
1·125	16	25·0	8·50	10·97	96	123
1·142	18	28·4	9·80	12·64	112	144
1·162	20	32·4	11·14	14·37	129	167
1·180	22	36·0	12·33	15·91	146	188
1·200	24	40·0	13·70	17·67	164	212
1·220	26	44·0	15·18	19·58	185	239
1·241	28	48·2	16·76	21·42	208	266
1·263	30	52·6	18·35	23·67	232	299
1·285	32	57·0	20·00	25·80	257	332
1·308	34	61·6	21·55	27·80	282	364
1·332	36	66·4	23·20	29·93	309	399
1·357	38	71·4	25·17	32·47	342	441
1·383	40	76·6	27·10	34·96	375	483
1·410	42	82·0	29·05	37·47	410	528
1·438	44	87·6	31·00	39·99	446	575
1·468	46	93·6	33·20	42·83	487	629
1·498	48	99·6	35·70	46·15	535	691
1·530	50	106·0	38·00	49·02	581	750

Sodium Bicarbonate.*—$NaHCO_3$ is obtained by passing washed carbon dioxide through a solution of sodium carbonate. If the solution is concentrated, the bicarbonate separates out as a crystalline powder; if it is dilute, large crystals are obtained. As carbonic acid is absorbed slowly by the solution, it is more advantageous to let it act upon crystallised or partly effloresced sodium carbonate. An intimate mixture is made of 1 part crystallised sodium carbonate and 4 parts of the effloresced salt or a mixture of equal weights of both, and it is saturated either with the carbonic acid of fermentation or with that obtained on burning lime. Where carbonic acid issues from the earth the process is greatly simplified. The bicarbonate of the ammonia-soda process generally contains ammonia.

In the production of sodium bicarbonate from ordinary soda crystals (dekahydrated) the product retains all the impurities of this material; hence Carey took the monohydrate as a starting-point. H. Gaskell and F. Hurter, of Widnes, went further, and converted the anhydrous neutral sodium carbonate into bicarbonate by simultaneous treatment with watery vapour and carbonic acid.

Sodium bicarbonate crystallises in monoklinic tables; it has a faintly alkaline reaction, and on exposure to 70° or in solution on boiling it loses half its carbonic acid and returns to monocarbonate. In dry air it is gradually converted into sesquicarbonate; 100 parts water dissolve at 0° 6·0 parts, and at 15° 8·85 parts of sodium bicarbonate. It is used for developing carbonic acid in the manufacture of effervescing drinks, in the preparation of unfermented bread (with hydrochloric acid, or acid calcium phosphate), for precipitating alumina from the solution of sodium aluminate (in the cryolite and bauxite industries), and in the preparation of baths for gilding and platinising. It has of late been proposed for ungumming silk and scouring wool, as it attacks the fibres less than soap or ammonia.

* Hydrocarbonate, carbonate of soda of pharmacy and cookery.

CHLORINE, CHLORIDE OF LIME, AND CHLORATES.

For obtaining chlorine, pyrolusite (manganese peroxide) is heated along with hydrochloric acid: $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. As developers there are used large stone-ware vessels, *A* (Fig. 308), fitted with a wide opening, *a*, for filling and emptying and with narrower tubulures, *b*, in which the delivery pipes are inserted. Heat is applied by means of steam. To this end, several such vessels are set in a chest, *B*, of wood or masonry, with a wooden lid, so that only the necks and the delivery-pipes project outside. The joints of the chest are carefully closed with clay or felt at *r*, in order to prevent the loss of the steam which is led into the chest from the boiler. The lye of manganese chloride is let out at *c*. On the large scale a trough is used, made up of plates of sandstone cemented together or hollowed out of a block of sandstone and saturated with hot tar.

If a mixture of manganese peroxide, salt, and sulphuric acid is used—

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2,$$

a strong heat is needed. A pan is used, the lower part of which, *b* (Fig. 309), is made of cast iron and the upper part, *d*, of lead; both parts are secured together at *a*.

At the Josephsthal paper works there is used a stout cast-iron pan, *A* (Fig. 310), its outflow pipe, *D*, being closed with a wooden plug luted in with clay. The lead

Fig. 308.

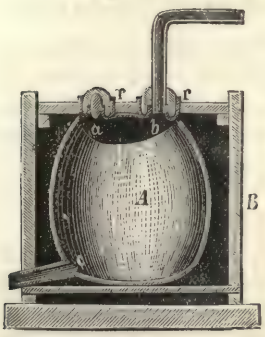


Fig. 309.

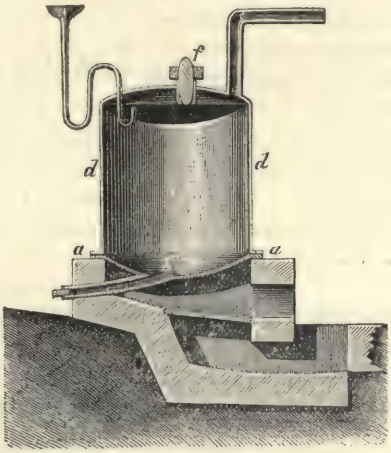
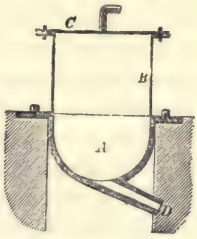


Fig. 310.



cylinder, *B*, which is screwed on, and the lid of which, *C*, carries the delivery-pipe, gives room for the materials to swell up. The production of chlorine takes place in *A*; the iron is but little attacked as long as an excess of manganese is present. When the pan is eaten through, a new one is quickly and inexpensively substituted. The lead cylinder is made very stout at the lower part, where it is most likely to be attacked. The upper part, which does not come in contact with the liquor, soon becomes coated with a dense layer of lead chloride, and is then no longer attacked. The spent liquor is run off at *D*, and the vessel is then well rinsed out with water.

For work on the large scale the recovery of the manganese is important.

Dunlop's process, which came into use at the St. Rollox works at Glasgow, is based upon the fact, first observed by Forchhammer, that carbonate of manganese, when heated to 260°, is converted into peroxide of manganese; that is, the carbonic acid is driven off, and the compound, $2MnO_2 + MnO$, obtained. The process consists in the following operations:—

1. Conversion of the manganese chloride into manganese carbonate.

2. Conversion of the carbonate into peroxide of manganese.

To the chlorine preparation residues, when they have become clear, either chalk or milk of lime is added to neutralise the excess of acid and precipitate the oxide of iron. This precipitate having settled, the clear liquid, a rather pure solution of manganous chloride, is poured into shallow troughs and intimately mixed with finely powdered chalk. The magma thus formed is transferred for further decomposition to a large cast-iron trough, 27 metres long by 3 metres wide. Parallel to the length of this vessel, a stout wrought-iron axle is carried, to which are fitted cast-iron branches serving as stirrers. The axle passing through stuffing boxes at each end of the trough gears with a motive power, whereby the stirrers are caused to keep the chalk constantly suspended in the manganese solution. High-pressure steam is conveyed into the trough and aids decomposition. The manganese carbonate obtained is freed from calcium chloride by washing, and, having been well drained, is calcined in a peculiarly constructed furnace, in which the carbonate is first dried on a higher stage, and then transferred to a lower and hotter stage, where oxidation is commenced. The oxidation is completed at the lowest stage of the furnace, to which plenty of air is admitted. The fire-place is constructed to admit of the regulation of the heat with great nicety, because too high a temperature would cause the formation of protosesquioxide, and too low a temperature would leave the carbonate undecomposed.

Gatty's Process.—In this process the residues are converted into manganese nitrate, which is next decomposed by heat. The residues are evaporated to the consistency of a syrup, and mixed with sodium nitrate:—

To 76 kilos, of manganese chloride
and to 95 kilos. of manganese sulphate } 106 kilos. of sodium nitrate are taken.

The mixture is dried, and then heated to a dull red heat in an iron retort, the fumes of nitric acid given off being used in the manufacture of sulphuric acid. The residue in the retort consists, according to the salt of manganese employed, of manganese peroxide, and sodium chloride or sodium sulphate; it may be lixiviated with water to obtain the manganese peroxide in a pure state if sodium sulphate is present.

The process of P. W. Hofmann has been described under the methods for the recovery of vat-waste.

Fr. Kuhlmann proposes to transfer the oxygen of the air at once to the manganous oxide. By heating manganese nitrate to 200° there are formed manganese peroxide and hyponitric acid. The escaping gases, mixed with air, are conveyed into recently precipitated manganous hydroxide, when a fresh quantity of manganese nitrate is formed—

$$Mn(OH)_2 + 2NO_2 + O = Mn(NO_3)_2 + H_2O,$$

which, when heated, furnishes anew manganese peroxide and hyponitric acid.

Weldon's Process.—Mr. Walter Weldon's process is performed by means of an apparatus comprising five vessels arranged at successive elevations, so that, after having been pumped up to the highest of them, the liquor operated upon can afterwards descend to all the others by its own gravity. The lowest of these vessels is a well, which is furnished with a mechanical agitator. The slightly acid chloride of manganese liquor with which the process commences runs from the stills in which it is produced into this well, and is there treated with finely divided calcium carbonate, the action of which is facilitated by energetic agitation. When the neutralisation of the free acid which is at first contained in this liquor and the decomposition of the iron and aluminium sesquichloride, which are also at first contained in it, are completed, the liquor is pumped up into settling tanks, placed nearly at the top of the apparatus, and known as the "chloride of manganese settlers." It now consists of a quite neutral mixed solution of manganese chloride and calcium chloride, containing in suspension considerable quantities of calcium sulphate, and small

quantities of ferric oxide and alumina. These solid matters rapidly deposit in the chloride of manganese settlers, leaving the bulk of the liquor perfectly bright and clear, and of a faint rose colour. The next step is to run off the clear portion of the contents of the settlers into a vessel immediately below, called the oxidiser. This is usually a cylindrical iron vessel about 12 feet in diameter, and about 22 feet deep. Two pipes go down nearly to the bottom of the oxidiser—a large one for conveying a blast of air from a blowing engine, and a smaller one for the injection of steam. The latter is for the purpose of raising the temperature of the contents of the oxidiser when necessary; for sometimes the chloride of manganese liquor reaches the oxidiser sufficiently hot—between 130° and 160° or 170° F. Immediately above the oxidiser is a reservoir containing milk of lime. The oxidiser having received a charge of clear liquor from the settlers, and this liquor having been heated up to the proper point if it was not already hot enough, blowing is begun, and milk of lime is then run into the oxidiser as rapidly as possible, until the filtrate from a sample taken at a tap placed nearly at the bottom of the oxidiser ceases to give a manganese reaction with solution of bleaching-powder. A certain quantity of milk of lime is then added, and the blowing continued until peroxidation ceases to advance. That point is usually attained when from about 80 to 85 per cent. of the manganese present has become converted into peroxide. The contents of the oxidiser are now a thin black mud, consisting of solution of calcium chloride containing in suspension about 2 lbs. of manganese peroxide per cubic foot, these 2 lbs. of manganese peroxide being combined with varying quantities of manganous oxide and lime. This thin mud is now run off from the oxidiser into one or other of a range of settling tanks or "mud settlers," placed below it, and is there left at rest until it has settled as far as it will, usually until about one-half of its volume has become clear. The clear part is then decanted, and the remainder, containing about 4 lbs. of manganese peroxide per cubic foot, is then ready to be used in the stills. There it reacts upon hydrochloric acid, liberating chlorine, with reproduction of exactly such a residual solution as was commenced with. With that solution the round of operations is begun again; and so on, time after time, indefinitely.

The extraordinary simplicity of the Weldon process ensures it the preference as against other methods aiming at the same object, and it is almost universally employed. According to Jetzler, the manganous hydroxide, after being washed in the air, is partly oxidised and then exposed to a current of hot air whilst suspended in the lime-lye. In this manner a more rapid and complete oxidation is effected and a dry manganese peroxide is obtained.

According to the more recent proposals of Weldon, the lyes of manganese chloride are evaporated and treated either separately or along with solid calcium, or magnesium chloride, or with magnesium or manganese manganite obtained in a former operation in a cylindrical retort, heated from without, and so arranged that at one end the powder is regularly and continuously introduced, whilst the solid product of the reaction is taken out at the other. The retort, *E* (Figs. 311 and 312), may be made of fire-clay, or of cast iron, or of both materials. It seems best to construct the retort of fire-clay for the chief part of its length, and only to make the part where the charge is introduced of cast iron for a short extent. The outer cylinder, *C*, can be made of wrought iron with a fire-clay lining. The whole rests and turns on the friction rollers, *D*. Through the pipes *F*, heating-gas enters from a generator into the annular combustion chamber, *X*, and the air necessary for combustion through the apertures, *e*. The heating-gas arrives in the immovable pipe, *J*, which is connected by the ring-shaped conduit, *a*, with the tubes *F*. Air enters through the tube *K* into the interior of the retort, *E*, and hereby the solid product of the reaction, manganese and magnesium manganite, is emptied. This evacuation is facilitated by wings placed

spirally, fixed on the axle, *n*. The gases, charged with the chlorine generated, escape through the tube, *N* which also serves for charging the retort. The axles, *n* and *o*, may be either immovable, or may turn in the opposite direction to the retort, *E*. The products of combustion issue from the ring-shaped combustion chamber, *X*, through the apertures, *H*, into the fixed smoke chamber, *P*. The manganite obtained is treated with hydrochloric acid for the production of chlorine; the lyes are evaporated down and mixed with a portion of the manganite; they are again conveyed into the

Fig. 311.

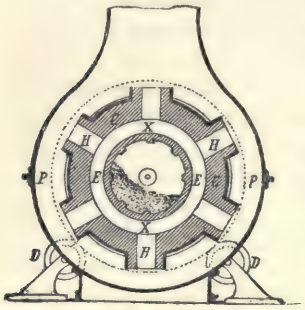
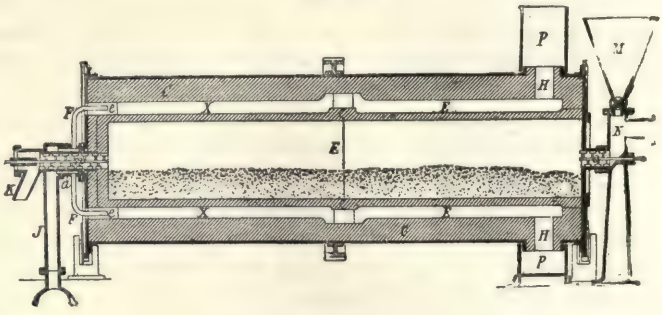


Fig. 312.



decomposition chamber, *E*. The hydrochloric acid is thus almost completely converted into chlorine. Working results on this modification have not yet been made known.

For the utilisation of the chlorine residues, Schaffner, of Aussig, precipitates the manganous chloride with lime, dries the precipitate, and calcines it in a reverberatory furnace, obtaining protosesquioxide of manganese, employed with iron ore in the blast furnace. The solution of calcium chloride simultaneously obtained is precipitated by sulphuric acid, yielding the material known as *annaline;* that is to say, the gypsum used in paper manufacture. In the process of soda-making from sodium and iron sulphides, as suggested by Malcherbe and improved upon by Kopp, for the oxides and carbonate of iron, the corresponding manganese compounds may be substituted. Carbonate of manganese may be used to convert sodium sulphide into soda, and may also serve for the preparation of permanganates. A. Leykauf suggests that the residues of chlorine manufacture should be employed to form a violet-coloured paint, known as Nuremberg-violet, a compound of ammonia, oxide of manganese, and phosphoric acid. In England the residues are frequently employed in the purification of coal-gas and as disinfectants.*

Of the processes for obtaining chlorine without manganese, the most important is that of Deacon, in which hydrochloric vapours are oxidised by atmospheric oxygen: $2HCl + O = H_2O + Cl_2$.

Deacon and Hurter found that the decomposition of hydrochloric acid by oxygen takes place at a much lower temperature if the gaseous mixture, instead of simply passing through ignited tubes or over porous substances, is led over heated salts of copper, lead (except the sulphate), or compounds of manganese. The most efficacious are the compounds of copper; so that, if a mixture of hydrochloric acid with an excess of atmospheric air is passed over porous bodies, soaked in solution of copper sulphate and heated to 360° to 400°, all the hydrochloric acid is burnt to chlorine and water. In this reaction, which begins at 260°, the copper sulphate remains unchanged unless the temperature is raised too high. Not until about 425° are formation and volatilisation of copper chloride perceptible. The power of resistance as well as the efficacy of the copper sulphate can be intensified by joining with it certain salts which are in

* Chlorine residues, as long as they were procurable, were an excellent agent for the precipitation and purification of sewage. See Slater, *Sewage Treatment*, p. 102.

themselves without action upon the gaseous mixture, *e.g.*, potassium or sodium sulphate. Numerous experiments showed the conditions for the decomposition between air and hydrochloric acid in presence of copper sulphate.

1. The quantity of the hydrochloric acid decomposed by 1 mol. copper sulphate in gaseous mixture of similar composition and at the same temperature depends upon how often the gaseous molecules pass through the sphere of activity of the copper sulphate.

2. For all velocities of the gases in transit the opportunity for efficacy is the same for long tubes of the same section in one and the same time.

3. In long tubes of different section the opportunities for action are alike when the speeds of the currents are inversely as the squares of the diameters of the tubes.

4. In porous masses the efficacy increases directly as the rapidity.

5. Circumstances being otherwise equal, the quantity of the hydrochloric acid decomposed varies with the square root of the number expressing the proportion between hydrochloric acid and oxygen.

6. At very high temperatures a little copper chloride is formed, but its quantity is in no proportion to the quantity of chlorine formed.

7. The efficacy of the copper salt extends to gaseous molecules not in contact with the salt; the decomposition of the hydrochloric acid takes place under circumstances in which no material exchange can take place between the copper salt on the one hand and the hydrochloric acid and air on the other.

In the technical execution of the Deacon process the hydrochloric acid is either prepared from sodium chloride and sulphuric acid in an ordinary salt-cake furnace or it is liberated from aqueous acid already obtained. On a small scale the latter is preferable, as in this manner it is always practicable to produce a current of hydrochloric acid of uniform strength, whilst the evolution of hydrochloric acid from the sulphate furnaces is very rapid at first and then becomes very slow. On the large scale this defect may be avoided by having several salt-cake furnaces in serial action, so that when the evolution declines in one the activity of the next begins. The gas obtained in either manner is immediately mixed with a quantity of air which contains more oxygen than suffices to convert all the hydrochloric acid into chlorine, and is passed through heated U-shaped tubes of cast iron, which supply the temperature required for the process. The composition of the gaseous mixture can be checked at any time by means of a small air-pump, which at every stroke of the piston forces a certain volume of the gas through a standard soda-lye coloured with litmus. The succeeding decomposition furnace consists of a cast-iron chest in which are chambers, each provided in its lower part with a grating, or false bottom. Upon this stand in the first chamber, and also in the second, upright drain-pipes which have been steeped in a hot concentrated solution of 2 mols. copper sulphate and 3 mols. sodium sulphate and dried. The other chambers are filled with fragments of brick or clay balls which have been treated in the same manner. The entire furnace is enclosed with an air-jacket and this again with a jacket of masonry traversed by fire-flues, serving to keep back a part of the radiant heat from being lost. Another part is restored in the process itself by the combustion of the hydrochloric acid. The pipes serve to prevent any obstruction of the apparatus by ferric oxide or chloride. It has been observed that, especially when an iron apparatus is used for producing and conducting hydrochloric acid, the acid always carries with it ferric chloride, from which it cannot be freed before it enters the decomposition furnace. In this it deposits the iron upon the copper sulphate, either as chloride, or, if the formation of chlorine has already set in, as pulverulent ferric oxide. This iron dust falls out of the drain-pipes through the grating into the space below, where it is easily removed. Deacon has recently removed the partition walls from the decomposition furnace.

After the gaseous mixture has passed through the decomposition furnace, it consists

of chlorine, nitrogen, water, excess of oxygen, and unburnt hydrochloric acid. The latter is eliminated as the gases (the temperature of which has been previously reduced by means of cold air) are passed through a scrubber charged with dilute hydrochloric acid and water. The gas is then freed from the accompanying water by a tower charged with calcium chloride, or preferably a coke-tower in which sulphuric acid trickles down, and it is then ready for use in the chloride of lime chambers. Of course the drying arrangement is superfluous if an aqueous liquid is to be saturated with chlorine, as in the preparation of potassium chlorate. For the latter purpose, Kunheim uses the chlorine obtained by Deacon's method. The chlorine is so completely absorbed by the milk of lime in its passage that mere traces are present in the escaping air. The draught in the entire plant is effected by any suction apparatus placed beyond the chloride of lime chambers.

Of other methods for producing chlorine, the following deserve notice:—

1. MacDougal, Rawson, and Shanks's process, consisting in the decomposition of calcium chromate by hydrochloric acid, the result being the formation of chromium and calcium chlorides, and the evolution of free chlorine—

$$2CaCrO_4 + 16HCl = Cr_2Cl_6 + 2CaCl_2 + 3H_2O + 6Cl.$$

158 parts of chromic acid yield 106 parts of chlorine. The chloride of chromium is again precipitated with carbonate of lime, and by ignition converted into chromate of lime. Only three-eighths of the chlorine contained in the hydrochloric acid is given up, while manganese yields one-half.

2. Vogel's method of decomposing chloride of copper by heat. 3 mols. of chloride yield 1 mol. of chlorine; according to Laurens the process is—

$$2CuCl_2 = Cl_2 + Cu_2Cl_2.$$

The chloride in the crystalline state is mixed with half its weight of sand, and heated in earthenware retorts to 200° to 300°, yielding chlorine gas, while the remaining protochloride of copper is re-converted into perchloride by the action of hydrochloric acid. Mallet has constructed a peculiar rotating apparatus for the decomposition of this salt, the same apparatus serving to prepare oxygen. 100 kilos. of cupric chloride yield 6 to 7 cubic metres of chlorine gas.

3. Péligot's method. When 3 parts of bichromate of potassa and 4 parts of concentrated hydrochloric acid are gently heated, the fluid yields, on cooling, crystals of bichromate of chloride of potassium, KCl,CrO_3; at 100° this salt yields chlorine.

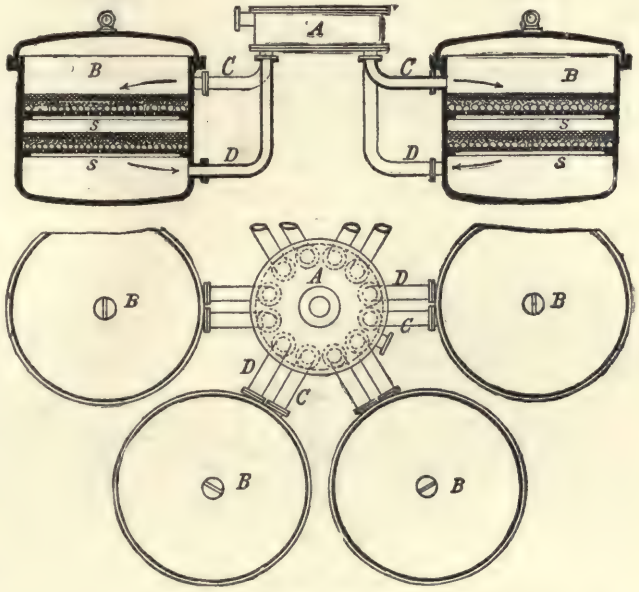
The production of chlorine from calcium and magnesium chlorides appears especially important, as, if this end is reached, the Leblanc process will probably be entirely superseded by the ammonia-soda process. Among the many attempts, those of Solvay and Pechiney demand especial attention.

Solvay ignites the residues of calcium chloride with clay. From the mass the carbonic acid is expelled by an addition of hydrochloric acid, and the organic matter is destroyed by heating in the air. To prevent the mass from caking together in the furnace there is added to the mixture of calcium chloride with silica or clay a sufficient quantity of the residues of former decompositions or of brickbats. It appears that sand is not adapted for the process, but a kind of infusorial earth, known in Belgium as "ergeron." Before entering the apparatus the air is passed through vessels containing pieces of caustic soda, so as to take up carbonic acid and moisture. The decomposition apparatus is made of iron, coated with a mixture of clay, soda, and nitrifiable matters.

The chlorine prepared in this manner is strongly diluted with air and nitrogen. To make it fit for the production of chloride of lime, the pulverulent slacked lime is spread out in layers of suitable thickness upon a bed of porous mineral matters—*e.g.*, gravel, flints, sand, or asbestos cloth. The layers of lime are laid methodically, as is done with the masses for purifying coal tar. The chambers may be arranged in series, but

in any case they must be placed so that the chloriferous mixture of gases may encounter the layer of lime in its whole thickness, and pass through from above downwards. Each of the six lead chambers, *B* (Figs. 313, 314), connected by the reverser, *A*, and arranged in a circle, is provided with two false bottoms, upon which is laid first asbestos cloth on a bed of gravel, and then the lime. The chloriferous gases enter the reverser, *A*, and pass from there through a pipe, *C*, into the upper part of the chamber *B* which has been longest in use. They pass downwards, first through the upper and then the lower layer of lime, and return through *D* to the reverser, passing thence to the upper part of the next chamber *B*, which they traverse in the same manner, and so on until they arrive at the chamber with the most recent charge of lime. Five chambers *B* are always in use, as the sixth is disconnected for emptying and refilling as soon as its contents are sufficiently strong.

Fig. 313. Fig. 314.



The process of Weldon and Pechiney has been at work for a year at Salindres, and promises to be of importance for the utilisation of magnesium chloride.

The solution is evaporated until it corresponds to the formula $MgCl_2.6H_2O$, and then mixed with 1·3 equivalent of MgO for the formation of oxychloride. For mixing there is used a revolving pan, *A* (Figs. 315 and 316), turning on rollers, *a*. Movement is taken from the driving belt, *B*, by means of the toothed wheel, *c*; the agitators, *C*, *D*, *E*, are driven in the same manner. The magnesia is introduced into the pan containing the concentrated magnesium chloride, with constant stirring. The oxychloride is formed with liberation of heat, and congeals to hard masses, broken into lumps by the stirrers.

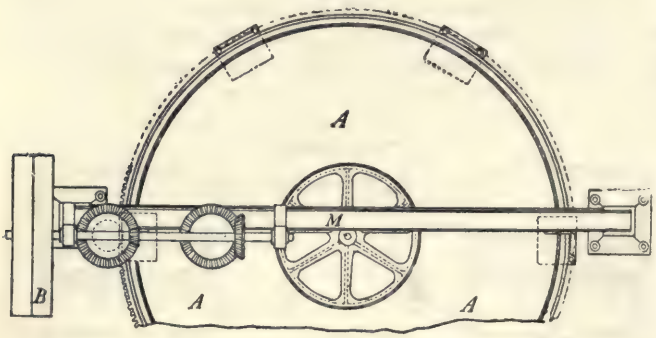
It has the following composition :—

$MgCl_2$	35·00; Cl = 26·16 per cent.
MgO	19·84
H_2O	41·16
Impurities	4·00

It is broken up and sifted. What passes through a sieve with meshes of 5 mm. is returned to the magnesium chloride for the further preparation of oxychloride. The granular oxychloride is dried. The temperature must not exceed 300°. At Salindres, Pechiney uses for a drying chamber a channel of masonry. The oxychloride is placed in seven layers, each of 5 to 6 cm. in thickness, upon small trucks, which are drawn through the heating channel as in Figs. 317 and 318. To keep out the external air on the admission of a truck, the door, *a*, is opened, the truck is pushed into the chamber *A*, and the door, *a*, is again closed. The slides, *c* and *d*, are then raised and the entire train of trucks drawn

forwards in the channel by the contrivance, *G*, so that the first truck partly enters the chamber *B*, and can be entirely drawn into it by the hook, *D*. It can be removed after lowering the slide, *d*, and opening the door. The gases at 300° enter at *M*, and leave the channel through the pipe, *N*.

Fig. 315



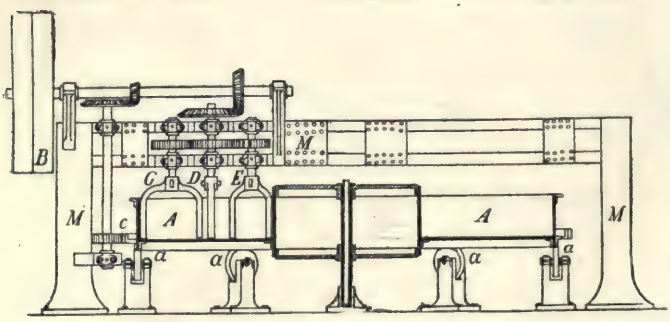


Fig. 316.

The measuring apparatus, *A*, of the filling arrangement (Fig. 319) is divided into seven compartments corresponding to the basins on the trucks. Each compartment can be closed below by a door, *a*. By turning the wheels, *C*, all these doors may be simultaneously opened or closed. Below the measuring apparatus is a hopper, *D*, movable on wheels and also divided into seven compartments contracted below. Underneath, on the height of the drying channel, there is a movable frame, *E*, to receive any empty truck. In Fig. 319 the frames and trucks are shown in a position ready to be loaded. Before the truck is brought into this position there are placed between each two basins two short iron partitions, *d*, which determine the thickness of the layer of oxychloride. The partitions are secured by the screws, *n*, the heads of which press against the cross rails, *o*, which form a part of

Fig. 317.

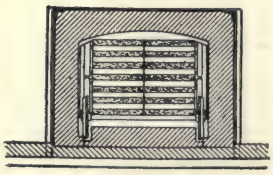
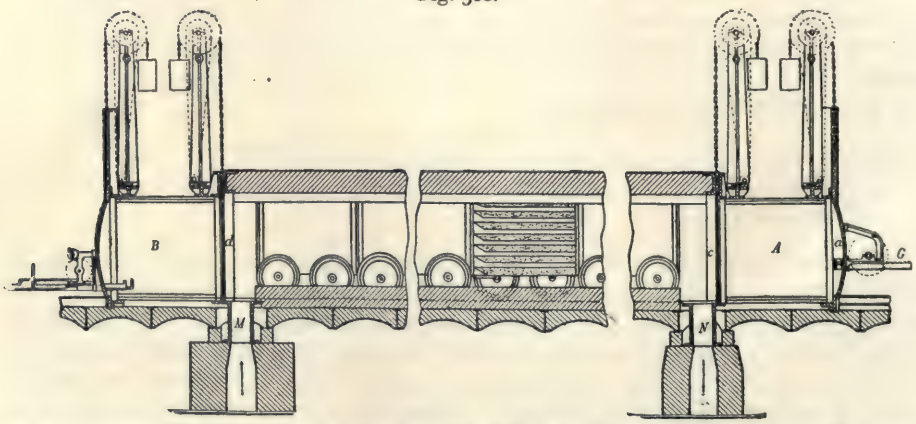


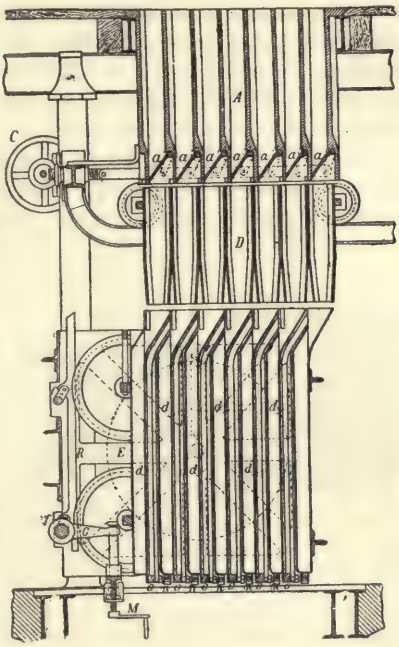
Fig. 318.



the partitions. To the movable frame there are fixed below two rails, *R*, upon which the truck moves. The rails are fixed to the levers, *F*, so that the truck can be raised

towards the top of the frame by turning the screw, *M*, which is in connection with the great lever, *G*; when the partitions have been introduced the frame is turned by means of a toothed wheel with a crank, which is only shown in dotted lines in the figure; the hopper is moved above it; the measuring apparatus is filled, and the contents are then emptied into compartments of the truck by turning the wheel, *C*. The frame is then turned, the partitions removed, and the truck moved into the drying stove.

Fig. 319.



The oxychloride loses up to 65 per cent. of water and 5 to 8 per cent. of the chlorine in the state of hydrochloric acid; 100 parts oxychloride of the above composition yield 73·36 per cent. of residue of the following composition:

$MgCl_2$	44·45; Cl = 33·30 per cent.
MgO	28·36
H_2O . . .	21·62
Impurities . . .	5·47

The decomposition of the oxychloride is effected in chambers, which are heated by gas generator fires. Each of the narrow work-chambers, *A* (Figs. 320 and 321), opens upward into the combustion chamber, *B*, and is fitted with an inspection slit, *q*. The movable regenerator turner, *D*, consists of cast-iron tubes divided into three compartments *i*, *o*, *u*. When the valve, *N*, is opened (Fig. 322), heating gas passes through the pipes, *V* and *C* (connected at *W*), into the compartments, *o*, to arrive by way of the pipe, *d*, in the combustion-chamber, *B*. The air needed for burning this heating-gas enters at the bottom of the compartments, *i* and *u*; rises in them upwards and issues from their

Fig. 320.

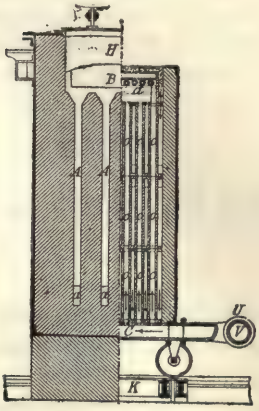
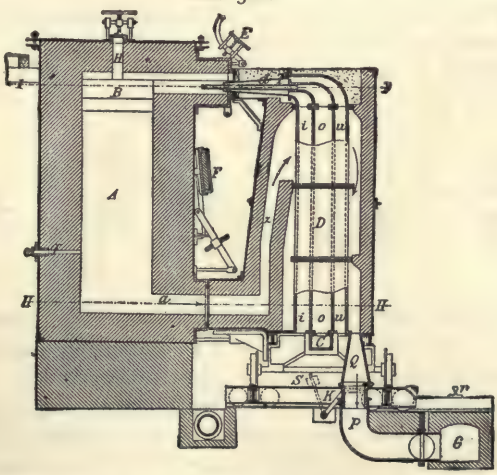


FIG. 321.



upper end through the broad, flat pipe, *T*, into the combustion chamber, *B*. The combustion gases go downwards through the working-chambers, *A*, then through the channels *a* and *z* and round the iron pipes, *D*, in order finally to escape, through *Q*

and *P*, into the channel *G*. For the easy connection of the burner with the pipe *P*, the piece, *Q*, can be raised or lowered by the lever, *S*. When the burner is in the position with respect to the furnace (properly speaking) which is shown in Fig. 321 the rails upon the block-truck, *K*, are fixed to other rails (of which one is shown at *r*, Fig. 321), in such a manner that the burner can be pushed over upon these other rails and be carried upon them to another block-truck opposite the next furnace. Whilst, therefore, in one furnace a solid substance giving off chlorine is being heated in a current of air, the movable regenerative burner can be used for heating the work-chambers of another similar furnace. As soon as these work-chambers are hot enough, the valve, *N*, is closed, the pipe *Q* is lowered and the block-truck, *K*, upon which the entire regenerative burner rests, is drawn away from the furnace until the wheels of the burner are opposite the rails. The openings for introducing the gases into the work-rooms must be closed by the door *E*, and the openings for removing the products of combustion from the working-chambers by the doors *F*. The doors *E* and *F*, when in the closed position, are pressed tightly by screws. The work-chambers, *A*, are now charged with magnesium oxychloride in small pieces by a tilting-truck, which, after being loaded, has been brought into the proper position upon the cover of the furnace. After the lid has been removed a hopper is placed over the opening *H*, and the oxychloride is shot into the hopper, so that it falls into the work-chamber *A*. The cover of the openings *H* is then quickly put on again, and air is admitted through several openings (not shown in Fig. 321) in the door *E* to *A*. The oxychloride is quickly heated by taking up a part of the heat previously stored up in the walls of the chambers, and there escapes from these chambers a mixture of gases and vapours containing chlorine and hydrochloric acid. This mixture goes from *A* through the channels *a* into the space between the masonry of the furnace and the door *F*, then through the channel *l* (Fig. 322) and the pipes, *m*, to corresponding arrangements for utilising the chlorine. When the decomposition of the oxychloride is sufficiently advanced, the access of air to the work-chambers is cut off; the door *F* is opened, and the residual oxide contained in the chambers *A* is taken out. The cover of the opening *H* is again put

FIG. 322.

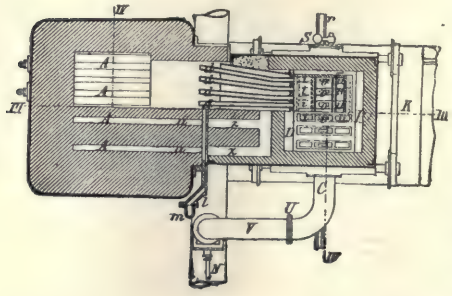
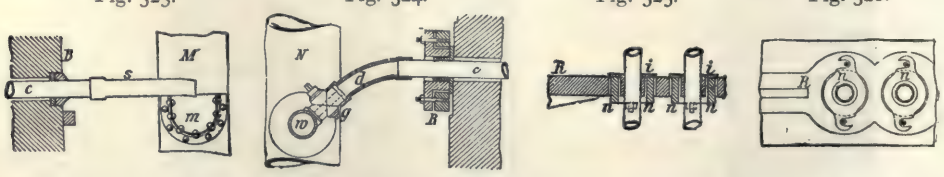


Fig. 323. Fig. 324. Fig. 325. Fig. 326.



in its place, and after opening the door *E*, the movable generative burner is brought back to the position shown in Fig. 321 when the work-rooms of the furnace (strictly so called) are again heated for the next operation.

A refrigerator is connected with the decomposition apparatus. It consists of a stone tower filled with glass tubes, through which cold water flows down. The glass tubes (Figs. 323 to 328) project with their ends from the sides of the tower. On one side, *A*, each tube is connected by a caoutchouc pipe with the main, *w*, which is supplied with water from the hollow column, *N* (Fig. 323). On the other side, *C*, the water flows through flexible pieces, *s*, into channels, *m*, from which it is carried off through

the hollow column, *M* (Fig. 223). That the glass tubes, *c*, may be less likely to break, they are kept always filled with water. As the acid liquid condensing on the surface of the tubes flows to the end, *A*, the joints here must be well closed. For this purpose there is on the end of the glass tube a short caoutchouc tube, *i*, with a flange (Figs. 325 and 326), which is firmly pressed against the stone by the tube-shaped part of the stuffing-box, *n*. The stuffing-boxes are drawn on by screws, which pass through the ring-shaped flanges, and catch in threads cut in the rail, *R*. The gases or vapours to be cooled are most conveniently introduced at *P*, near the cover of the tower, and escape

Fig 327.

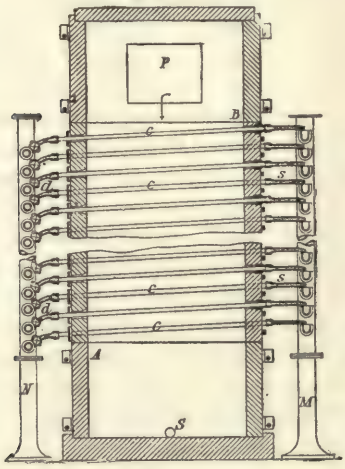
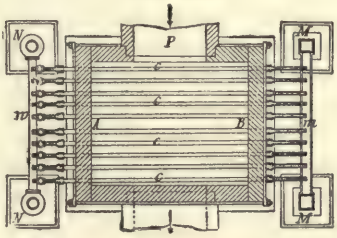


Fig. 328.



near the bottom, on the opposite side. The liquid condensed in the tower runs out through the opening *S*.

The mixture of nitrogen, superfluous air, chlorine, and hydrochloric acid is let out of the decomposition apparatus through this tube-cooler by means of two gasometer bells dipping into a solution of calcium chloride and moving alternately up and down, then through a number of sandstone vessels, and lastly through a scrubber. The hydrochloric acid in the gases is thus completely condensed, and a mixture of chlorine and air is carried on. The hydrochloric acid from the various condensers is mixed and marks on the average 17° Tw.

Of 100 parts of the chlorine of a charge, 15 parts remain in the residues, 45·23 are evolved as free chlorine, and 39·77 parts form hydrochloric acid. As about 7 parts are lost in drying, the original 100 parts of chlorine are distributed as follows :—

Loss in drying	6·60	per cent.
Left in residues	14·00	,,
Free chlorine	42·25	,,
Chlorine as HCl	37·15	,,

As a further loss of 5 per cent. is admitted the result is—

Loss	on drying	6·27	11·27	per cent.
	general	5·00		
Cl returned to process	residues	13·30	48·59	,,
	as HCl	35·29		
Free chlorine obtained		40·14		,,

To obtain 40·14 free chlorine there must be produced 100 − 48·59 = 51·51 parts of chlorine.

The yield will probably be increased by improvements—*e.g.*, by heating more strongly. The residue, after the decomposition in the furnace, is placed in vessels cooled by water and provided with agitators.

The refrigeration is quickly effected. The mass is then sifted ; about $\frac{6}{7}$ pass through the sieve, being almost completely decomposed and containing scarcely 4 per cent. of chlorine. The part remaining on the sieve, about $\frac{1}{7}$ of the mass, is still solid oxychloride, slightly decomposed. The chlorine is about 40 per cent. This part of the residue is

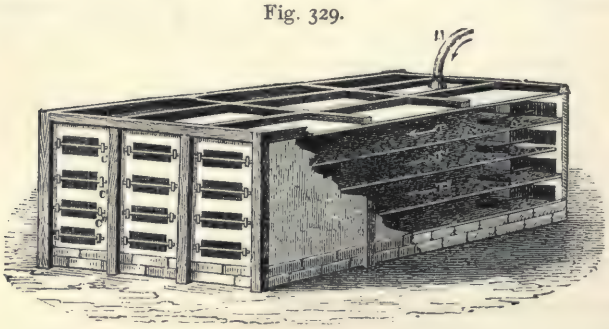
at once returned to the furnace, whilst the magnesia (at Salindres) is dissolved in hydrochloric acid, and is again submitted to the process.

At Salindres there are at work (December 1887) two fires with eight chambers each. A thousand kilos. of chlorine ought to be produced in twenty-four hours, but the present yield is 720 to 760 kilos. The author states that at Stassfurt 200,000 tons of magnesium chloride yearly are allowed to flow into the river, so that a ton of chlorine ought to be produced decidedly cheaper at Stassfurt than it is now in England.

Properties and Uses of Chlorine.—At the ordinary temperature and pressure of the atmosphere chlorine is a greenish-yellow gas, its sp. gr. = 1·33; it possesses a peculiarly disagreeable, irritating odour, and is soluble in water, 1 volume absorbing 2·5 volumes of gas, forming the well-known *aqua chlorii*, or *acidum muriaticum oxygenatum aqua solutum* of the pharmaceutists, and the chlorine water of the scientific chemist. The bleaching property of chlorine gas, shared also by its solution, is due to the great affinity of chlorine for hydrogen, so that the chlorine, while seizing upon the hydrogen of the organic body, in most instances causes the simultaneous decomposition of water, and by the formation of ozone destroys the organic colouring matter, hydrochloric acid being formed at the same time, a fact requiring attention in the use of chlorine as a bleaching agent. When linen, or rather flax, raw cotton, and paper pulp are bleached by chlorine, the fibre, really cellulose, is not acted upon, but only the colouring matter is oxidised by the ozone formed. Chlorine cannot be used to bleach animal matters, or such as contain nitrogen, these becoming yellow by its action. Chlorine is not suited for transport either as gas or in aqueous solution, therefore one of its combinations with oxygen and a base, viz., a hypochlorite, is used. Hydrated oxide of calcium or slaked lime is the chief constituent of bleaching-powder. Usually the alkali manufacturers prepare bleaching-powder.

Chloride of Lime.—In the production of chloride of lime the chlorine passes from the generator through the tube, M, Fig. 329, into a room constructed of large blocks and slabs of sandstone joined by means of asphalt cement, or a mixture of coal-tar and fire-clay. Sometimes the room is built of bricks laid in a similar cement, the interior being lined with asphalt; leaden chambers also are used for this purpose. The room is fitted with several shelves upon which slaked lime is placed in layers of 3 to 4 inches and more in thickness. The chlorine gas is readily absorbed, heat being evolved. Care is to be taken that the temperature does not exceed 25°, because then calcium chlorate is formed; this is prevented by admitting the gas slowly. As soon as the absorption ceases, the bleaching-powder is removed with rakes from the shelves, and fresh lime introduced. Frequently the chloride of lime is somewhat diluted by an admixture of slaked lime.

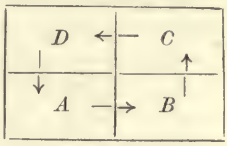
Fig. 329.



Chloride of lime, on a system involving the use of several chambers, has been successfully manufactured at the Lari alkali works at Petrowitz for eighteen months. According to L. Jahne, the system consists of a lead chamber, 2 metres in height, divided by cross walls into four completely distinct compartments. The chlorine is supplied from three sandstone generators, placed at a suitable distance, having a

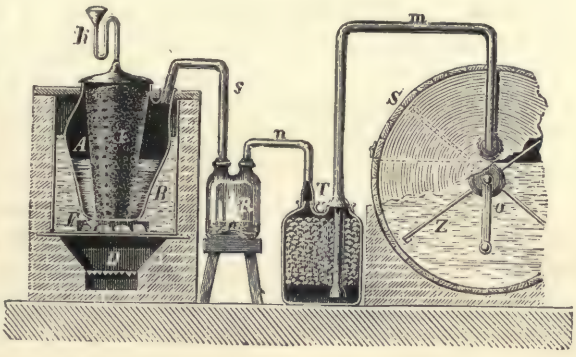
common delivery-pipe, and which are charged and emptied at equal intervals of time, so that a uniform current of chlorine is always supplied to the chambers. Each of the four chambers, *A* to *D* (Fig. 330), has at that corner of the top which is nearest to the middle of the system, a pipe for the removal of the chlorine, and at the angle diagonally opposite a longer escape-tube. In each chamber there is also, besides the working door and the opening at the bottom for withdrawing the finished product, a bell for observing the gases, a thermometer, and an opening for taking samples. The ends of the eight entrance and exit tubes and the chlorine main, open into a reversal apparatus, and there are arranged accordingly three chief exit-pipes which open through a lead main into the chimney. The connection of the ends of the various tubes is effected by placing a leaden ball over each two ends, so that the chlorine main in the middle is connected with the entrance-pipe of *A*, the exit-pipe of *A* with the entrance-pipe of *B*, the exit of *B* with the entrance *C*, &c.

Fig. 330.



Liquid Chloride of Lime.—When it is desired to prepare a solution of chloride of lime, the apparatus shown in Fig. 331 is employed. Two or four earthenware vessels, *A*, about 2 hectolitres capacity, are placed in the leaden trough, *B*, the bottom of which is protected by a cast-iron plate and a stoneware slab, *F*, from the direct action of the fire at *D*. *B* represents a concentrated solution of calcium chloride serving the purpose of a bath, such a solution boiling at 179·5°. By the syphon funnel, *K*, the hydrochloric acid is poured into *A*. *I* is a perforated cistern filled with manganese. *S* is the leaden gas tube. The chlorine, being first washed in *R*, passes through *n* into *T*, filled with pieces of manganese, to decompose any vapours of hydrochloric acid carried over, and, lastly, the chlorine passing through *m* reaches the absorption vessel, *S*. This vessel is a lead-lined wooden cask, fitted with an axle bearing spokes to which are fastened gutta-percha floats. The bearings and plummer-blocks of the axle are made of guaiacum wood and ebonite. The axle, *o*, gears with a suitable motive power, the purpose being to keep the milk of lime in continuous motion while the gas is being admitted.

Fig. 331.



The chlorine gas enters above the level of the fluid, which is kept constantly stirred, to assist in the absorption. From the vessel wherein the absorption takes place a small tube leads into another vessel filled with water to a depth of 18 to 24 centimetres; a tube fitted to this vessel leads into the open air to convey away any unabsorbed chlorine. As in the preparation of solid chloride of lime, it is here necessary to guard against an increase in temperature and also saturation; Schlieper has proved that too concentrated solutions evolve oxygen, while too dilute solutions yield calcium chlorate.

Numerous researches have been published on the *Formation of Chloride of Lime.* In the chlorination of lime the presence of water is of capital importance, though there exist the most contradictory views. Graham, and subsequently Frike and Reimer, maintained that an anhydrous calcium hydrate was incapable of chlorination. Göpner thinks an excess of 8 per cent. the most favourable, but by no means sufficient (?). Richters

and Junker recommend an excess of water of 1 to 2 per cent. Davis recommends 3 to 4 per cent. Kopfer obtained chloride of lime on chlorinising lime imperfectly slaked. Lunge and Schäppi show that imperfectly slaked lime may be chloridised, and that only ½ mol. water of hydration may be communicated to the chloride of lime, according to which the great absorption of chlorine is intelligible—

$$2Ca(OH)_2 + 2Cl_2 = 2CaOCl_2.H_2O + H_2O; \text{ and}$$
$$CaO + H_2O = Ca(OH)_2.$$

It has not been found possible to chlorinate a perfectly anhydrous caustic lime, which goes against Göpner's formula. Chloride of lime containing 42 to 43 per cent. of effective (bleaching) chlorine can be easily obtained; thus any formula which regards such proportions as exceptional becomes untenable. The strongest chloride of lime is prepared with dry chlorine and a hydrate of lime containing 2 to 4 per cent. excess of water. If the chlorine is imperfectly dried, an excess of 1 to 2 per cent. is most favourable. The formation of calcium chloride is unimportant.

Scheurer-Kestner gives the highest temperature in normal working as 55°, Hurter as 40°, Gmelin as 18°, and Bobierre as 50°. On using moist chlorine, Schäppi obtained at—

Temperature.		Effective Chlorine.
−17°	...	2·30
0	...	19·88
7	...	33·24
21	...	35·50
21	...	39·50
30	...	40·10
40	...	41·18
45	...	40·50
50	...	41·52
60	...	39·40
90	...	4·26

Hence it is an error to suppose that hydrate of lime cannot absorb chlorine at 0°, as, after two hours' action, a 20 per cent. chloride was produced, and a weak sample was even obtained below 0°. With dry chlorine the most favourable temperature is 10° to 16°; with moist chlorine, 20° to 60°, though the action is best between 40° and 45°. The residue obtained on dissolving chloride of lime in water consists chiefly of calcium hydroxide, as appears from the following analysis of a good sample:—

CaO . . .	39·89	$2CaOCl_2 + H_2O$.	82·65
Bleach do. . .	43·13	$CaCO_3$. . .	0·95
Cl as $CaCl_2$. .	0·29	$CaCl_2$. . .	0·44
H_2O . . .	17·00	$Ca(OH)_2$. .	6·80
CO_2 . . .	0·42	H_2O (free) . .	9·82
	100·73		100·66

The latest experiments by Lunge confirm the formula $CaOCl_2$ for chloride of lime.

The bleaching salts obtained from the bivalent metals, calcium, strontium, and probably barium, have probably the nature of double salts of the formula Cl...R...OCl, in which all the chlorine can be directly replaced by carbonic acid.

Properties of Chloride of Lime.—Chloride of lime is a white powder, the bleaching constituents of which dissolve in about 10 parts of water, whilst the excess of lime is undissolved. The bleaching action is manifested only on the addition of an acid.

The loss of value of chloride of lime on preservation in casks at temperatures from 5° to 17° was examined by J. Pattinson. Three sorts of chloride of lime had on January 29, 1885 (I.), and, after being kept for a year in casks, on January 5, 1886 (II.), the following respective compositions:—

	A.		B.		C.	
	I.	II.	I.	II.	I.	II.
Effective chlorine	37·00	33·80	38·30	35·10	36·00	39·20
Cl as chloride	0·35	2·41	0·59	2·42	0·32	1·97
Cl as chlorate	0·25	—	0·08	—	0·26	—
Lime	44·49	43·57	43·34	42·64	44·66	43·65
Magnesia	0·40	0·34	0·31	0·36	0·43	0·38
Ferric oxide	0·05	0·05	0·04	0·04	0·02	0·02
Alumina	0·43	0·35	0·41	0·36	0·33	0·35
Manganic oxide	trace	trace	trace	trace	trace	trace
CO_2	0·13	0·80	0·30	1·48	0·48	1·34
Silicates	0·40	0·50	0·30	0·04	0·50	0·50
Water	16·45	18·15	16·33	17·20	17·00	18·89
Total chlorine	37·60	36·24	38·97	37·52	36·58	34·87

Chlorometry.—As only the chlorine which exists in chloride of lime in the form of $CaOCl_2$ comes into play in its applications, such quantity determines its value.

Gay-Lussac makes use of the oxidising action of chloride of lime upon arsenious acid, a volume of dry chlorine gas dissolved in water being employed. The solution of chlorine is poured into a graduated tube divided into 100 parts, each of these divisions corresponding to one-hundredth of chlorine. A solution of arsenious acid in dilute hydrochloric acid is also prepared, the strength of the solution being such that equal bulks of the two liquids suffer mutual decomposition:—

$$\left.\begin{array}{l}\text{Arsenious acid, } As_2O_3,\\ \text{Water, } 2H_2O,\\ \text{Chlorine, } 2Cl_2,\end{array}\right\} \text{ yield } \left\{\begin{array}{l}\text{Arsenic acid, } As_2O_5,\\ \text{Hydrochloric acid, } 4ClH.\end{array}\right.$$

Water is decomposed; its oxygen combines with the arsenious acid, forming arsenic acid, while the hydrogen combines with the chlorine. Usually 1 litre of dry chlorine gas is dissolved in 1 litre of distilled water. The normal solution of arsenious acid is so prepared that it is entirely decomposed by the chlorine water to arsenic acid. The test is carried out as follows:—Take 10 grammes of the sample, and triturate with distilled water, adding sufficient of the latter to make up a litre. Next take, by means of a graduated pipette, 10 c.c. of the arsenious acid solution, and pour it into a beaker, adding a drop of indigo solution to impart a faint colour; next add, by means of a burette, sufficient of the bleaching-powder solution to cause the colour nearly to disappear, then add more of the indigo solution, and again bleaching-powder solution, until the fluid becomes quite colourless. The normal arsenious acid solution is prepared by dissolving 4·4 grammes of this acid in 32 grammes of hydrochloric acid, the liquid to be diluted to 1 litre. If 10 grammes of bleaching-powder contain 1 litre of chlorine gas, it is of 100° strength.

Penot's Test.—Penot has modified Gay-Lussac's method in the following particulars:—For the arsenious acid solution he substitutes sodium arsenite, and for the indigo solution a colourless iodised paper, which is turned blue by the smallest quantity of free acid. The paper is prepared in the following manner:—1 gramme of iodine, 7 grammes sodium carbonate, 3 grammes of starch, and $\frac{1}{4}$ litre of water are mixed. When the solution becomes colourless, it is diluted to $\frac{1}{2}$ litre; in this fluid white paper is soaked. The arsenical fluid is prepared by dissolving 4·44 grammes of arsenious acid, and 13 grammes of crystallised sodium carbonate in 1 litre of water. This solution is poured, by means of a burette, into the solution of the chloride of lime intended to be tested (10 grammes of the sample to 1 litre), the completion of the reaction being known by the paper remaining uncoloured. Mohr, again, has modified this process, not, however, in very essential particulars.

Wagner's Method.—This test, discovered in 1859, is the so-called *iodometrical method*, and is based upon the fact that a solution of chloride of lime separates the

iodine from a weak (1 to 10) and slightly acidified potassium iodide solution, the iodine being quantitatively estimated by means of sodium thiosulphate:

$$\left.\begin{array}{l}\text{Iodine, } 2I,\\ \text{Sodium thiosulphate, } 2Na_2S_2O_3 + 5H_2O,\end{array}\right\} \text{ yield } \left\{\begin{array}{l}\text{Sodium iodide, } 2NaI,\\ \text{Sodium tetrathionate, } Na_2S_4O_6,\\ \text{Water, } 5H_2O.\end{array}\right.$$

The test is thus executed: 100 c.c. = 1 gramme of bleaching-powder solution, obtained by dissolving 10 grammes of chloride of lime in 1 litre of water, are mixed with 25 c.c. of solution of iodide of potassium acidified with dilute hydrochloric acid. The ensuing clear, deep brown coloured solution is treated with sodium thiosulphate solution until quite colourless. The sodium thiosulphate solution is composed of 24·8 grammes of that salt to 1 litre of water; 1 c.c. of this solution neutralises 0·0127 gramme of iodine and 0·00355 gramme of chlorine.

G. Lunge's method for determining the bleaching chlorine in chloride of lime depends on the observation that hypochlorous acid if mixed with hydrogen peroxide immediately gives up its active oxygen, as does the hydrogen peroxide itself, so that we obtain a double quantity of oxygen. A turbid solution of chloride of lime is obtained in the ordinary manner with 10 grammes of the sample to 250 c.c. of water. 5 c.c. of the solution (= 0·2 gramme chloride of lime) are drawn off with a pipette, and this is let flow into the external space of the decomposition bottle of the nitrometer. Into the interior tube there is poured an excess of hydrogen peroxide; for this purpose 2 c.c. of the commercial article are sufficient. The quantity need not be accurately measured, and the proportion of actual hydrogen peroxide does not need to be determined as long as it is in excess. The little bottle is then fixed upon the caoutchouc stopper, grasping it by the neck, so as to avoid warming it; the cock of the nitrometer is then turned so as to connect the little bottle with the measuring tube, the mercury in which has been previously fixed at 0°. The bottle is inclined so that the liquids mix; it is shaken for a few moments, the mercury in both tubes is placed at the same level, and the result is read off. If 0·2 gramme chloride has been used, each c.c. of gas at 0° and at a pressure of 760 mm. represents 5 French degrees or 1·632 per cent. of efficient chlorine. If we dissolve 7·917 grammes chloride of lime in 250 c.c., and use for each test 5 c.c. of the solution, 1 c.c. of gas represents 2 per cent. chlorine.

The determination of bleaching chlorine—*i.e.*, of free HOCl or NaOCl, is also effected by titration with sodium arsenite. According to Penot, it is not usual to titrate back with solution of iodine, but to ascertain the end of the reaction by spotting. Here all the HOCl and NaOCl are converted into NaCl; it is therefore quite unnecessary to resort to other reducing agents, such as zinc powder, &c. We have in the sodium arseniate now present an indicator for the next operation, which even surpasses potassium chromate.

For determining the total chlorine present as hypochlorite and chloride, a part of the liquid obtained in the last operation is titrated with decinormal silver nitrate until the reddish-brown colour of silver arseniate appears.

For determining the chlorate another portion of the liquid obtained in the former operation (which contains no hypochlorite, but all the chlorate) is boiled in the valve flask with a strong solution of ferrous sulphate, the value of which with permanganate has been accurately ascertained, and, after cooling, it is titrated back with permanganate.

Chlorometric Degrees.—In Germany, Britain, Russia, and America the strength of chloride of lime is expressed in degrees, which give the percentage of effective chlorine; in France (and in some German works) the degrees represent the number of litres chlorine gas, at 0° and at a pressure of 760 mm., which can be liberated from 1 kilo. of the sample in question. The following table gives the chlorometric degrees for France and for Britain and Germany:—

French Degrees.		English and German Degrees.	French Degrees.		English and German Degrees.
65	...	20·65	100	...	31·80
70	...	22·24	105	...	33·36
75	...	23·83	110	...	34·95
80	...	25·42	115	...	36·54
85	...	27·01	120	...	38·13
90	...	28·60	125	...	39·72

The percentage may be calculated from the French degrees by multiplying the latter with 0·318 (1 litre chlorine gas weighs 3·18 grammes).

Chloride of Alkali.—A solution of hypochlorite of potassa is known in commerce under the name of *Eau de Javelle*, while the corresponding soda solution is known as *Eau de Labarraque;* these solutions are prepared by passing chlorine gas into a solution of either caustic (1) or carbonated (2) alkali—

(1) $2NaOH + Cl_2 = NaOCl + NaCl + H_2O$;

(2) $2Na_2CO_3 + Cl_2 + H_2O = NaOCl + NaCl + 2NaHCO_3$;

or by exhausting bleaching powder with water, and precipitating the solution with sodium sulphate or carbonate solution, calcium sulphate or carbonate being thrown down, while the hypochlorite and chloride of the alkali remain in solution.

Aluminium hypochlorite, or Wilson's bleaching liquor, is obtained by mixing chloride of lime solution with aluminium sulphate; it acts by evolving oxygen, leaving aluminium chloride in solution. Hypochlorite of magnesia (Ramsay's or Crouvelle's bleaching liquor) is obtained by adding magnesium sulphate to a solution of bleaching powder; the result is the formation of a very energetic bleaching compound, which, especially for the purpose of bleaching finely woven fabrics, as muslins, &c., is preferable to chloride of lime on account of the absence of caustic lime. Varrentrapp's bleaching salt, or zinc hypochlorite, is another energetic bleaching compound obtained by treating a solution of chloride of lime with zinc sulphate, the result being the precipitation of calcium sulphate, while zinc hypochlorite remains in solution; zinc chloride may be employed, but, of course, the solution then retains calcium chloride. Hypochlorite of baryta is sometimes used, hypochlorous acid being obtained by the addition of very dilute sulphuric acid.

Potassium Chlorate (*Chlorate of Potassa*).—This salt ($KClO_3$) consists, in 100 parts, of 38·5 of potassa and 61·5 of chloric acid; its crystals are rhombic and tabular in form. It formerly was prepared by passing chlorine gas into a concentrated solution of potassium carbonate, the result being the formation of potassium chlorate and chloride. As the chlorate is the less soluble it crystallises first, while by evaporation the mother liquor yields potassium chloride. The chlorate is then washed with cold water, and purified by recrystallisation. 100 kilos. of potassium carbonate yield in this manner 9 to 10 kilos. of the chlorate. At the present day, however, potassium chlorate is prepared by a method, a suggestion of the late Dr. Graham. Chlorine is caused to act at a high temperature upon milk of lime, with the result of the formation of calcium chlorate and chloride, the calcium chlorate being afterwards decomposed by potassium chloride. The method by which potassium chlorate is prepared on the large scale according to this plan is the following:—1 mol. of potassium chloride and 6 mols. of hydrate of lime, having been mixed with water, are submitted to the action of chlorine gas; the solution yields on evaporation crystallised potassium chlorate, while calcium chloride remains.

According to Lange there are used for saturating the milk of lime two mutually connected cylinders lined with lead, and provided with agitators (compare Fig. 331). Both are connected with each other and with the chlorine generator in such a manner that the contents of the one approach saturation, whilst the chlorine left unabsorbed in the other is taken up by fresh milk of lime. As soon as complete saturation is reached

in the first cylinder fresh milk of lime is substituted for the contents, and the current of chlorine is turned so that it first enters the second cylinder. The lye of calcium chloride and chlorate obtained has a rose-red colour, which some chemists refer to permanganic acid, and others to ferric acid, as it appears when manganese has been used. The colour is the sign of perfect saturation even where the chlorine (as at Kunheim's works at Berlin) is obtained by the Deacon process. The red liquid after settling is mixed with potassium chloride, concentrated down to sp. gr. 1·28, and let crystallise. The mother liquor from the first crop of crystals is again concentrated to sp. gr. 1·35, when a second, though smaller, crop of potassium chlorate is obtained. About 12 per cent. of the chlorate remains in the mother liquor, which consequently has to be worked up for chlorine. The crystals obtained contain calcium chloride and iron as impurities. To remove these the crude chlorate is dissolved in the smallest possible quantity of hot water; to 10 hectolitres of the liquid there are added 2½ kilos. of soda, and the solution after settling is let crystallise. For the formation of chlorate a small excess of chlorine is necessary, but a special application of heat is not needed, as the heat developed during reaction is sufficient.

Calcium chlorate is also formed by evaporating a solution of chloride of lime to dryness, and is then converted into the potassium salt by adding potassium carbonate or chloride. Old chloride of lime, which has partly lost its bleaching power, contains calcium chlorate, and may be used in the manufacture of potassium chlorate.

According to Muspratt, a solution of chlorine in milk of magnesia is evaporated down to 60°–98° Tw., so that, on cooling, a portion of magnesium chloride crystallises out. This lye is decomposed by the addition of potassium carbonate with formation of potassium chlorate and magnesium chloride. The bulk of the former crystallises out. The mother liquor still retains 5 to 10 per cent. of the potassium chlorate, which is not worth extraction. This lye is now further treated with hydrochloric acid and steam. The potassium chlorate is then decomposed into potassium chloride, with liberation of chlorine, which is absorbed by means of magnesia or lime. The solution, which contains hydrochloric acid in excess, is neutralised with magnesium carbonate, and forms then a solution of magnesium chloride, with a very slight impurity of potassium chloride, and in Germany would have very little value. But as the yield is larger than with the lime process, the magnesia process deserves more attention.

Properties.—Potassium chlorate crystallises in leaflets of a nacreous lustre, permanent in the air, which dissolve in 16 parts of water at 15°, in 8 parts of water at 35°, and in 1·6 part of water at 100°. If heated they give off oxygen, and if rubbed together with combustible matter they explode most violently. One kilo. potassium chlorate, if strongly ignited, or if heated with 0·5 kilo. pyrolusite or 1 kilo. ferric oxide, yields 391 grammes or 274 litres oxygen. It is extensively used in pyrotechny, in percussion caps, &c., as a constituent of the white gunpowder of Augendre and other explosives, for preparing permanganates, as an oxidising agent in tissue-printing—*e.g.*, in the production of aniline-blacks, and recently to a large extent in obtaining violet colours from dimethylaniline. In the production of aniline-blacks a few per cents. of potassium chlorate are added to the colour, and, after printing, the black is fixed by steam at 3–4 atmospheres. At this temperature the chlorate in contact with the organic matter is decomposed, when there occurs an oxidation, and sometimes a destruction, of the colouring matter, though generally the colour is rendered brighter and more beautiful. In the alizarine works in the transformation of sulphanthraquinonic acid into sodium alizarate, potassium chlorate is added to the melt to prevent the reduction of the alizarine.

Potassium Perchlorate ($KClO_4$).—This salt is sometimes used in pyrotechnics as a substitute for the more dangerous chlorate. It is obtained by cautiously heating the

chlorate until the mass becomes pasty. It is separate from the potassium chloride formed simultaneously by recrystallisation from hot water.

BROMINE.

Bromine is found in sea-water, which contains about 0·06 gramme per litre. The mother liquor of many brine-springs—*e.g.*, those of Schoenebeck (near Magdeburg), those of the basins of the Ohio and the Kanawha, especially at Mason City, Pomeroy, and Parkersburg, at Alleghany and Monongahala, in Western Pennsylvania, as well as the mother liquors from working the salts of Stassfurt and Leopoldshall, are so rich in bromine that its extraction is remunerative. In order to prevent admixtures of chlorine, the mother liquor of sp. gr. 1·32, containing 0·15 to 0·35 per cent. bromine, is mixed with dilute sulphuric acid, when hydrobromic and hydrochloric acids are liberated; the mixture is heated to 120°, thus separating the volatile hydrochloric acid from the less volatile hydrobromic acid which remains in the liquid. On cooling, sulphates separate out. The acid liquor, separated from the crystals, is distilled with manganese peroxide and sulphuric acid. As a receiver are used two Woulff's bottles, the first of which is empty, whilst the second contains soda-lye. In the first are condensed water, some bromine, bromoform, bromine chloride, and carbon bromide, whilst the bromine vapours pass into the second bottle, and dissolve there as sodium bromide and bromate. The lye is evaporated to dryness, the residue ignited (to convert the bromate into bromide) and distilled with sulphuric acid and pyrolusite, thus yielding pure bromine, which is best collected and preserved under concentrated sulphuric acid.

According to the process of A. Frank, the distillation of the bromine mother liquors with pyrolusite and sulphuric acid is effected at Stassfurt in large cubical stone vessels containing 3 cubic metres, and braced together with iron bars. At some distance from the ground there is introduced a perforated plate of the same stone upon which the pyrolusite is laid in pieces of the size of a nut. This vat is covered with a plate of the same material, which is lifted by means of a rope, with a counterpoise passing over a pulley. In this plate there is a stoneware pipe for the admission of steam; it is provided with a man-hole and an opening for introducing the bromine-lye and the dilute sulphuric acid. There is another aperture for the escape of bromine vapours. The stones after a time allow the solution of manganese chloride to ooze through, and have to be coated with tar. This introduces a new defect: the hydrocarbons of the tar are converted into bromine substitution-compounds, and thus considerable quantities of bromine are lost, and the product is rendered impure. The loss at every new tarring is estimated at 50 kilos. of bromine. A kind of stone has since been discovered at Porta, Westphalia, which does not require this costly preparation, and can be used at once.

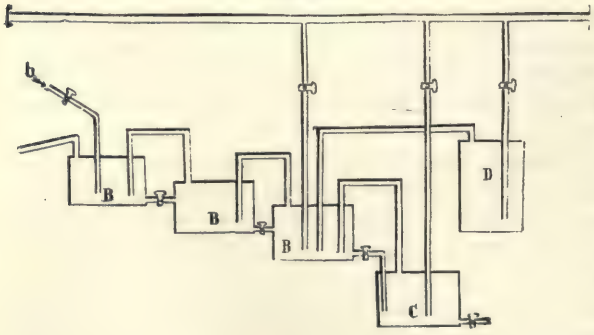
The bromine-lyes are placed in a large cistern situate above the distilling vessels, in which they can be warmed by a steam-pipe. Not all kinds of manganese are fit for this use, that of a medium hardness being the most suitable. The rest of the charge, both the bromine-lye and the acid, is run in through one of the small apertures in the stone lid, which is then immediately closed with a clay ball held down with iron weights. As soon as the apparatus is duly closed, steam is allowed to enter, when abundant vapours of bromine escape through the leaden pipe fitted in the second aperture of the stone plate. This lead pipe leads to a cooling worm of stoneware, surrounded by cold water, in which the bromine is condensed. The lower end of the worm opens into the middle tubulure of a large three-necked Woulff's bottle, in which bromine and bromine water collect. In one of the lateral tubulures there is a movable glass syphon, by means of which the bromine water can be drawn off into stoneware

jugs. In the other tubulure there is a bent glass tube, which passes down to the bottom of a conical iron vessel which widens upwards, and which is filled with water and iron borings. The vapours of bromine which have escaped condensation in the bottle combine with the iron. The impure iron bromide thus obtained, as well as the bromine water drawn off, are returned to the distilling apparatus for the next operation.

In the distillation there escapes at first scarcely anything but bromine; towards the end of the operation there appears bromine chloride, and, ultimately, when there is no more bromine present, pure chlorine passes over. These three stages of the operation can be easily distinguished by the colour of the gas in the glass receivers. In regular work the process is continued only to the first appearance of bromine chloride. An operation which takes two hours yields from 2 to $2\frac{1}{2}$ kilos. of bromine.

In this process for obtaining bromine the apparatus must be emptied after each operation and residues, still containing bromine and chlorine, contaminated with salts of manganese, &c., must be run off. Instead of the single distillatory vessels charged with bromine-lye, Frank employs a series of stills placed like stairs, and directly above each other, B (Fig. 332), connected by pipes and cocks. Into the uppermost of these vessels the lye, serving for the production of bromine, enters through the pipe, *b*, whilst into the lowest there passes a current of chlorine and steam, which is evolved in separate generators, either by the introduction of steam into the chlorine generator, D, or by conveying the two conjointly by means of pipes or by drawing the chlorine by means of the current of steam. They are mixed and distributed in the bromine-lye. The chlorine and steam entering the lowest vessel liberate the bromine from its compounds, and drive it, partly as pure bromine, partly as bromine chloride, and mixed with some free chlorine, into the next higher still, containing fresher lye, and so on through the entire column. Both the free chlorine and the chlorine in the bromine chloride, in as far as it is present, are absorbed, and in decomposing the bromine compounds present in the lyes and at the end of the column there escape merely vapours of bromine (nearly pure) and steam to the condensers. The number of the stills depends on their size and on the quantity and the strength of the lye to be operated upon. As soon as the lowest still is sufficiently driven off, its contents pass into the dechlorinising vessel, C, which is at a lower level, and is connected by means of pipes and cocks. In this process the mother liquor is of course free from the salts of manganese, &c., which interfere with the treatment of the residues from the ordinary process.

Fig. 332.



In the apparatus used at the United Chemical Works of Leopoldshall the bromine-lye flows through the tube, *a*, fitted with a hydraulic joint into a drum, *b*, of fire-clay or sandstone extending transversely through the entire width of the tower, which is provided on each side with a row of openings directed obliquely downwards. Below this drum there is a horizontal sandstone plate, *e*, well cemented into its place, in which are cemented conically shaped earthern pipes, cut off obliquely below and provided with a slit above (Figs. 333 and 334). They are fixed with the oblique point downwards, whilst the upper part is free and projects to the same height above the plate.

These pipes are so fixed that each stream of liquid issuing from the openings of the drum, *b*, falls in the place between two ranks of the tubes. The lye distributes itself equally above the plates, flows through the slits of the tubes and out at their points in fine streams upon the balls, which fill the tower nearly to the top. The vapours given off are led through the tube *o* of the stoneware worm, placed in the cooler, *p*, and the liquefied bromine collects in the bottle, *q*. In the recipient, *B*, there lie four sandstone

Fig. 333.

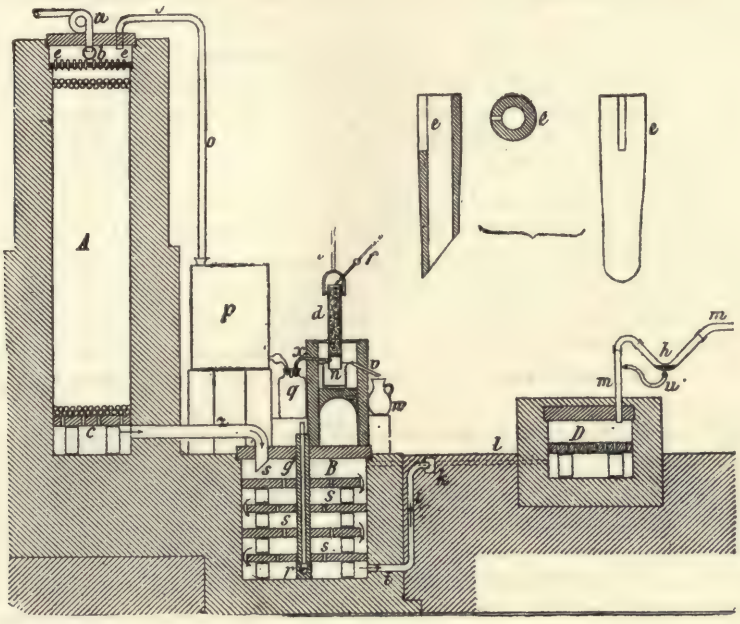


Fig. 334.

plates, *s*, above each other, joining close up to three of the walls, but leaving a small interval against the fourth wall. The intervals are alternately on two opposite sides, and each plate is provided with a row of fine holes. In the middle of the apparatus there is a short sandstone pipe which can be connected above with the steam pipe, and which penetrates all the sandstone plates. It is placed close up to another short sandstone pipe, *r*, which lies on the bottom and extends straight through the apparatus, and is bored longitudinally, and is also fitted with lateral openings arranged at regular intervals. The lye trickling through the tower, *A*, collects beneath the sieve-like false bottom, *c*, arrives from here through the tube *z* in the apparatus, *B*, and flows zigzag downwards over all the plates in the direction indicated by the arrows, in order to pass from the bottom through the ascending pipe, *i*, into the exit channel, *k*. The apparatus is constantly kept full of liquid to the point of the tube *z*. At the same time steam is led in through the pipe *g*, and keeps the lye constantly boiling. The vapours rise chiefly through the holes of the plates, *s*, and thus compel the lye to take its way over the plates through the slits. By this apparatus the lye is completely freed from small adhering traces of free chlorine and bromine. The vapours collect in the upper part of the apparatus, mix there with the chlorine arriving from the washing apparatus, *D*, through the tube *l* (shown in the figure by dotted lines), rise through the tube *z* (which offers a sufficient transverse section), back into the tower, *A*, which they traverse from below upwards. Into the vessel, *n*, there plunges a stoneware pipe, *d*, suspended by a strap to the rod, *t*, so as to admit of turning. Above the entrance of the tube *x* lies a perforated false floor, and upon it a charge of iron filings. These are covered with a second false bottom, upon which a slight current of water is passed

through the pipe *f*. The vapours not condensed in the cooler, *p*, pass from below into the moistened iron turnings; all the chlorine and bromine are absorbed, and the lye dropping off flows continually through the tube *v*, into the receiver, *w*, whilst air and watery vapour escape freely from the top of the tube *d*. For the production of the uniform current of chlorine which is necessary, the tubing, *m*, connected with the chlorine generator is bent at right angles. At its lowest point, a glass tube, *h*, provided with a tubulure, is inserted, so that the small quantity of condensed water which here collects escapes through the flexible pipe, *u*, connected with the tubulure into the washing apparatus, *D*.

Crude bromine when obtained by the earlier process always contains chlorine, even when, as it is done at Stassfurt, the Woulff's bottle is slightly warmed towards the end of the operation, so as to drive the volatile bromine chloride into the iron borings. It must therefore be submitted to rectification. This takes place in glass retorts containing about 15 litres each, the necks of which are cemented into glass receivers, surrounded with cold water. Each retort is placed in a small special sand bath, so that if a retort bursts the damage may be as limited as possible. Only a small watery fraction contains chlorine; it is removed and returned to the stone vats.

At Stassfurt bromine is sent off in strong glass bottles with ground stoppers. The stoppers are covered over with melted shellac, then luted with clay and tied with parchment paper. Four or twelve such bottles are packed in a box. Stassfurt and Leopoldshall furnish yearly about 300 tons of bromine, and North America about 200 tons.*

Properties and Applications of Bromine.—Bromine as a liquid appears in mass of a dark reddish brown, but in thin layers of a hyacinth red. Its odour is strong, and resembles that of chlorine. Bromine is rather freely soluble in water but more readily soluble in solution of potassium bromide, in hydrobromic acid, and in hydrochloric acid—in the last-mentioned liquid 13 per cent. The aqueous solution is reddish brown, and on exposure to light it is decomposed, like chlorine water, with the liberation of oxygen and the formation of hydrobromic acid. At 15° 100 parts of bromine water contain 3·226 parts of bromine. With water, bromine forms at 0° a solid, crystalline hydrate. Bromine dissolves readily in ether, alcohol, chloroform, and hydrogen sulphide. In aqueous sulphurous acid it dissolves, forming hydrobromic acid; it boils at 63° and is converted into dark-red vapour. At 7·2° bromine forms a reddish-brown crystalline mass. With colouring-matters bromine behaves like chlorine. It turns organic matters brown. Like iodine, potassium bromide, ammonium and cadmium bromide, and potassium hypobromate, it is used in photography and pharmacy. In the form of bromethyl, bromamyl, and brommethyl, it serves in the production of certain coal-tar colours, *e.g.*, Hofmann's blue. Since 1874 bromine is used in the production of eosine (tetrabromfluoresceine). It is also used as a disinfectant. Cinnabar, blende, and copper pyrites are decomposed and dissolved by bromine.

IODINE.

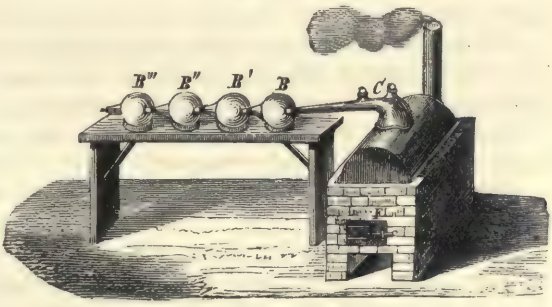
Iodine was discovered in 1811 by Courtois in a lye obtained from sea-weeds. The first iodine manufactory was set up by Tissier, at Cherbourg, in 1824. It occurs in sea-water and is taken up by marine plants. In the crude nitre of South America it is found in large quantity, and in smaller proportions in some brine springs. The presence of iodine in the phosphorites of Amberg in Bavaria and of Diez (on the Lahn), as also in the French departments of Lot and of Tarn and Garonne, may possibly become

* This latter quantity could be indefinitely increased if the demand were greater, which would be the case if better means of transport could be adopted. Shippers fear it, and the freight is consequently high.

of commercial importance. Kuhlmann of Lille obtains iodine as a lye-product in preparing superphosphate from French phosphorites, which in 1000 kilos. contain ½ kilo. of iodine. The chief seat of the iodine manufacture is at Glasgow, where there are twelve works. There are two in Ireland, and ten to twelve in the Department of Finisterre in France, and also in Asturias. At Tarapaca in Peru, and Antofagasta in Bolivia, iodine is obtained in very considerable quantities from the mother-liquors of the nitre works.

In order to obtain iodine from sea-weeds, the latter are first converted into kelp, that is to say, they are incinerated, the product broken to pieces and lixiviated with water, leaving an insoluble residue of 30 to 40 per cent., and yielding to the liquid 60 to 70 per cent. This solution, having a sp. gr. of 1·18 to 1·20, contains chlorides, sulphates, and carbonates of alkalies, potassium sulphide, chloride, and iodide, and hyposulphites of alkalies; by evaporating and cooling the liquor, the potassium sulphate and potassium and sodium chlorides are removed. To the remaining mother-liquor, previously poured into shallow open vessels, dilute sulphuric acid is added, the result being, that while a strong evolution of gases, sulphuretted hydrogen, and carbonic acid takes place, there is formed a thick scum and a deposit of sulphur at the bottom of the vessel; the sulphur when washed and dried is sold. When the evolution of gas has completely ceased, more sulphuric acid is added, and, according to Wollaston's method, the required quantity of manganese; this mixture is poured into a large leaden distilling apparatus, *C*, Fig. 335. By this means the iodine is set free, carried over in the state of vapour to the receivers, B, B′, B″, and condensed as a solid crystalline mass. In Paterson's large iodine works at Glasgow this operation is carried on in a cast-iron hemispherical vessel of 1·3 metre diameter, the cover being a leaden dome, to which are fitted two earthenware still heads, connected by means of porcelain tubing with two earthenware receivers, Fig. 335, each consisting of 4 to 5 parts. At Cherbourg, iodine is obtained, according to Barruel's plan, by passing chlorine gas into the mother-liquor; by this plan the iodine is separated from the iodide of magnesium, the latter taking up chlorine instead—

Fig. 335.



$$(MgI_2 + Cl_2 = MgCl_2 + I_2).$$

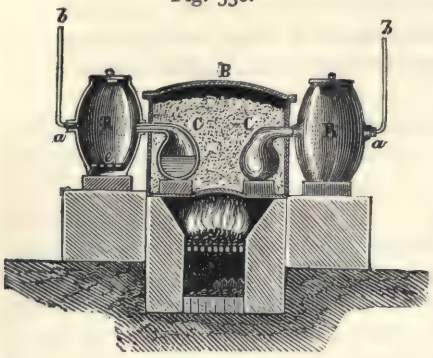
A more recent method, by which all the iodine present in the mother-liquor is obtained, consists in distilling the liquor with chloride of iron—

$$(2NaI + Fe_2Cl_6 = 2I + 2NaCl + 2FeCl_2).$$

As iodine is only very slightly soluble in water, 1 part of iodine requiring 5524 parts of water at 10° to 12° for its solution, that is, 1 grain of iodine to 12 ounces of water, it is carried over with the steam and deposited at the bottom of the receiver in the form of a black powder. When iodine is prepared by the aid of chlorine, the quantity of gas should be exactly sufficient to decompose the iodide of magnesium, for if the quantity of chlorine be too small no iodine is separated; and if too large, chloride of iodine is formed and free bromine, both of which, being volatile, escape. The iodine when removed from the receivers is drained on porous bricks or tiles, and dried between folds of blotting-paper. It need hardly be said that the iodine should not come in contact with a metallic surface. The iodine thus obtained has to be purified by sublimation, an operation carried on in the apparatus represented in Fig. 336, consisting

of stoneware retorts, C C, placed in the sand-bath, B, heated as shown in the woodcut. Each of these retorts is filled with upwards of 40 lbs. of crude iodine, and entirely surrounded by sand in order to prevent the sublimation of any iodine in the necks of the retorts. These are then connected with the receiver or condenser, R R, in which the crystalline iodine is deposited, the tubes, *a b*, *a b*, being for the purpose of carrying off the watery vapour. 1 ton of kelp yields on an average 4·07 kilos. of iodine.

Fig. 336.



Allary and Pellieux evaporate the sea-weed lyes after separating the potassium chloride and sulphate and roast the residue to oxidise the sulphur compounds. The residue is lixiviated, the solution evaporated, pulverised and extracted with alcohol. The alcohol is distilled off and the residue, consisting of potassium and sodium iodide in a saturated solution, is mixed with a quantity of potassium carbonate equivalent to the sodium iodide present, and treated with carbon dioxide. There are formed potassium iodide and sodium carbonate which is converted into bicarbonate and deposited. The residual solution of potassium iodide is neutralised with hydrochloric acid and recrystallised from alcohol in order to eliminate traces of potassium chloride.

Vitali saturates the sea-weeds with a solution of potash so that on incineration no iodine may be lost. The ash is heated to redness with potassium dichromate. The yield is said to be much greater than after treatment with chlorine.

The process of Stanford is carried out on the large scale by the British Sea-weed Company, at Dalmuir, near Glasgow.

To prevent losses Pellieux lets the fresh weeds ferment before incineration in shaft furnaces.

The crude nitre of Chili and Bolivia contains 0·059 to 0·175 per cent. iodine in the state of sodium iodate, besides traces of sodium and magnesium iodide. The mother-liquors from refining the crude nitre and converting it into potash saltpetre are treated for iodine by passing in a current of SO_2 until the iodine begins to redissolve. Latterly nitrous acid is preferred to sulphurous. The iodine liberated is dried and refined by sublimation. The iodine present as iodides is precipitated by means of chlorine. One litre of the mother-liquors from refining nitre contains 2·3 to 4·8 grammes iodine.

At Peruana in Tarapaca the concentrated lyes of sodium saltpetre have the following composition:—

Sodium nitrate	28
„ chloride	11
„ sulphate	3
Magnesium sulphate	3
Sodium iodate	22
Water	33
	100

The quantity of the solution of sodium bisulphite necessary for precipitation depends on the proportion of iodine present. The two liquids are mixed by means of a mechanical agitator, when the iodine falls to the bottom of the vat as a black mud. Flakes of iodine, which rise to the surface, are skimmed off with wooden ladles and put in settling vats. The mother-liquor thus chiefly freed from iodine is run off into a deep receiver, and is first treated for nitrate. It is afterwards again treated

for iodine. The iodine mud deposited at the bottom of the precipitating vat is repeatedly washed with clean water, filtered and converted by means of a filter-press into blocks of 0·2 metre in thickness. This crude iodine contains 80–85 per cent. pure iodine, 5–10 per cent. of fixed matter, and 5–10 per cent. of water. It is distilled in an iron retort, connected with eight stone-ware receivers, each 0·9 metre long and 0·75 metre in diameter. The last is closed with a wooden cover, luted on with clay, as are all the joints of the apparatus. The sublimed iodine is packed in small pitched kegs.

Iodine has recently been brought into commerce in the form of copper iodide, obtained by treating the lyes with a mixture of sodium bisulphite and copper sulphate.

Properties and Uses.—Iodine (I = 127; sp. gr. = 4·94) is a black-grey coloured crystalline substance, with a metallic appearance not unlike graphite. On being heated iodine is converted into vapours which, according to Stas, when concentrated exhibit a blue colour, and a violet in a more dilute state. Iodine fuses at 115°, and boils above 200°. It is somewhat soluble in water, readily so in alcohol, ether, hydriodic acid, potassium iodide solution, carbon disulphide, chloroform, benzol, aqueous solution of sulphurous acid, and solution of sodium thiosulphate. A solution of iodine imparts a violet colour to starch. Adulteration of iodine with either pulverised charcoal or graphite may be at once detected by treating a sample with alcohol or a solution of sodium thiosulphate, in each of which the iodine, if pure, ought to dissolve completely, leaving no residue on sublimation. Sometimes the weight of iodine is fraudulently increased by the addition of water. Iodine is largely used in photography in the form of potassium iodide; for the preparation of other iodine compounds, for instance, mercury iodide; also in the preparation of some of the tar colours, iodine violet, iodine green, and cyanine blue, the latter a compound of iodine and lepidin, a volatile base. The total production of iodine in Europe and Chili amounted in 1869 to 3453 cwts., more than half, or 1829 cwts., being produced in Scotland and Ireland. At the present day the production of iodine at the South American nitre works is estimated at 300 tons yearly. Scotland and Ireland now produce 130 tons, and France 50 tons.

Iodine is also used in the production of eosine, blue shade (tetraiodofluoresceine). According to the analysis of Wanklyn (1872) the iodine of commerce contains—

	Good.		Inferior.
Iodine . . .	88·61	...	76·21
Chlorine . . .	0·52	...	0·88
Ash	0·72	...	1·11
Water	10·15	...	21·80
	100·00		100·00

NITRIC ACID AND NITRATES.

Soda Saltpetre.—This salt, $NaNO_3$, known as cubic nitre, Chilian and Peruvian saltpetre, is found in the middle regions of the rainless district of the west coast (*costa seca*) of South America, most abundantly between 19° and 24° S. Lat. The chief localities are in the southern extremity of Peru, in the province Tarapaca, on the barren coasts of Bolivia, and the desert of Atacama. It is found in beds (*caliche* or *tierra salitrosa*) of ¼ to 1½ metre in thickness, extending for more than 240 kilometres to the neighbourhood of Copiapo in the north of Chili. The beds are covered with clay, and consist almost entirely of clean, dry, hard salt, and have apparently been formed from sea-weed.

The superjacent rock (*lostra*) is from ½ to 2 metres thick, and consists chiefly of a hard conglomerate of sand, felspar, porphyry, and other minerals. The composition

of the caliche varies. It contains from 48 to 75 per cent. sodium nitrate, 20 to 40 per cent. sodium chloride, and undetermined quantities of sodium sulphate, calcium sulphate, potassium nitrate and iodate, magnesium chloride, as well as insoluble matter, and organic substances including guano. It is broken up in a disintegrator, and placed in dissolving pans. Some of the works operate in open, quadrangular cisterns; those better arranged use closed, egg-shaped pans, provided with two movable covers, the one for introducing the caliche and the other for taking out the spent mineral. The mass rests upon a perforated false bottom at about one-quarter the height of the pan, and which consists of four pieces movable on hinges. The pans are filled up to the top with comminuted caliche, mother-liquor is run in to half height, and heat is applied by means of steam. In $1\frac{1}{4}$ to $2\frac{1}{2}$ hours the lye is sufficiently saturated with nitre, and is run off into settling vats. After standing for some hours, the clear lye is let flow into flat crystallisers. The residue in the pan is removed. The crystals formed, after the mother-liquor has drained off, are spread out in layers of 0·3 to 0·5 metres in thickness upon a large floor (*Cencha*) exposed to currents of air, and dried by frequent turning.

Sodium Nitrate.—This salt, also known as cubical saltpetre, Chili-saltpetre, nitrate of soda, $NaNO_3$, containing in 100 parts 36·47 soda, and 63·53 parts nitric acid, is found native in the district of Atacama and Tarapaca, near the port of Iquique, in Peru. The deposit chiefly consists of the pure, dry, hard salt, and is close to the surface of the soil. It is also found in other parts of Peru mixed with sand, in some places close to the surface of the soil, in others at a depth of 2·6 metres. Valparaiso being the great exportation depot for Peru, Bolivia, and Chili, both surface and deep soil salts are met with in the trade of that important port. The unrefined Chili saltpetre is crystalline, brown or yellow, and somewhat moist; but the salt sent to the European markets is commonly semi-refined by being dissolved in water and evaporated to dryness. The composition of a sample in 100 parts is:—

Sodium nitrate	94·03
Sodium nitrite	0·31
Sodium chloride	1·52
Potassium chloride	0·64
Sodium sulphate	0·92
Sodium iodide	0·29
Magnesium chloride	0·93
Boric acid	traces
Water	1·96
	100·00

Being deliquescent the salt is not employed in the manufacture of gunpowder, but may be used for blasting powder. It is largely used for the preparation of sulphuric and nitric acids; for purifying caustic soda; for making chlorine in the manufacture of bleaching powders; for the preparation of sodium arseniate; in the curing of meat; in glass-making; in the preparation of red lead; in large quantities in the conversion of crude pig-iron into steel, by Hargreave's and by Heaton's processes; for preparing potassium nitrate; and for the preparation of artificial manures and composts, it being also used unmixed as a manure for grain crops.

It may be seen from the analysis of nitrate of soda quoted above that that salt contains a small quantity of iodine, which at Tarapaca is extracted from the mother-liquor remaining from the re-crystallisation. According to M. L. Krafft the iodine amounts to 0·59 gramme in 1 kilo. of crude nitrate; 40 kilos. of iodine being prepared per day. M. Nöllner thinks that the formation of the nitre deposits in Chili and other parts of South America has taken place under the influence of marine plants containing iodine. In order to give some idea of the large and increasing exportation

of Chili saltpetre, we quote from the published statistics, that in 1830, 18,700 cwts., and in 1869, 2,965,000 cwts., were shipped.*

Potassium Saltpetre.—($KNO_3 = 101{\cdot}2$. In 100 parts, 46·5 parts potassa, and 53·5 parts nitric acid.)—This salt is to some extent a native as well as a chemical product. The well-known flocculent substance often observable on walls, especially those of stables, is composed in a great measure of nitrates; a similar phenomenon is seen in subterranean excavations, and even in many localities the surface of the soil is covered with an efflorescent saline deposit, consisting largely of potassium nitrate. These deposits are most common in Spain, Hungary, Egypt, Hindostan, on the banks of the Ganges, in Ceylon, and in some parts of South America, as at Tacunga in the State of Ecuador; while in Chili and Peru nitrate of soda, so-called Chili saltpetre, is found in very large quantities under a layer of clay as above-mentioned.

Occurrence of Native Saltpetre.—Although native saltpetre is met with under a variety of conditions, they all agree in this particular, that the salt is formed under the influence of organic matter. As already stated, the salt covers the soil, forming an efflorescence, which increases in abundance, and which if removed has its place supplied in a short time. In this manner saltpetre, or nitre as it is sometimes called, is obtained from the slimy mud deposited by the inundations of the Ganges,† and in Spain from the lixiviation of the soil, which can be afterwards devoted to the raising of corn, or arranged in saltpetre beds for the regular production of the salt. The chief and main condition of the formation of saltpetre, which succeeds equally in open fields exposed to strong sunlight, under the shade of trees in forests, or in caverns, is the presence of organic matter—viz., humus—inducing the nitre formation by its slow combustion; the collateral conditions are dry air, little or no rain, and the presence in the soil of a weathered crystalline rock containing felspar, the potassa of which favours the formation of the nitrate of that base. All the known localities where the formation of nitre takes place naturally, including the soil of Tacunga, formed by the weathering of trachyte and tufstone, are provided with felspar. The nitric acid is due to the slow combustion of nitrogenous organic matter present in the humus, it having been proved that the nitric acid constantly formed in the air in enormously large quantities by the action of electricity and ozone, as evidenced by the investigations of MM. Boussingault, Millon, Zabelin, Schönbein, Froehde, Bottger, and Meissner, has nothing whatever to do with the formation of nitre in the soil; a fact also supported by Dr. Goppelsröder's discovery of the presence of a small quantity of nitrous acid in native saltpetres.

Mode of Obtaining Saltpetre.—The mode of obtaining saltpetre in the countries where it is naturally formed is very simple, consisting in a process of lixiviation with water, to which frequently some potash is added for the purpose of decomposing the nitrate of lime occurring among the salts of the soil, the solution being evaporated to crystallisation. Soils yielding saltpetre are termed Gay earth or Gay saltpetre. The process by which nitrate of potassa is naturally formed is imitated in the artificial heaps known as saltpetre plantations, formerly far more general than at the present time, it having been found that the importation of Indian saltpetre, and the manufacture of potassium nitrate by conversion from sodium nitrate, are cheaper sources. Thus, saltpetre beds are to be met with only under peculiar conditions, as, for instance, in Sweden, where all landed proprietors are required to pay a portion of their taxes in saltpetre.

The mode of making these plantations may be briefly described as follows:—Materials containing much carbonate of lime—for instance, marl, old building rubbish,

* The exports from Chili to Europe were, in 1882, 410,000 tons, and in 1883, 530,000 tons.

† The mud of the Ganges contains, after exposure, 8·3 per cent. of potassium nitrate and 3 per cent. calcium nitrate. The yearly export of saltpetre from India is 25,000 tons.

ashes, road scrapings, stable refuse, or mud from canals—is mixed with nitrogenous animal matter, all kinds of refuse, and frequently with such vegetable substances as naturally contain nitrate of potassa, such as the leaves and stems of the potato, the leaves of the beet, sunflower plants, nettles, &c. These materials are arranged in heaps of a pyramidal shape to a height of 2 to 2½ metres, care being taken to make the bottom impervious to water by a well puddled layer of clay, the heap being in all directions exposed to the action of the atmosphere, the circulation of which is promoted through the heap by layers of straw. The heap is protected from rain by a roof, and at least once a week watered with lant (stale urine). The formation of saltpetre of course requires a considerable length of time, but when, taught by experience, the workmen suppose a heap *ripe*, the watering is discontinued, the salt containing saltpetre soon after efflorescing over the surface of the heap to 6 to 10 centimetres in thickness; this layer is scraped off, and the operation repeated from time to time until the heap becomes decayed and has to be entirely removed. In Switzerland saltpetre is artificially made by many of the farmers, simply by causing the urine of the cattle, while in stable in the winter time, to be absorbed by a calcareous soil purposely placed under the loose flooring of the stables, which are chiefly built on the slope of the mountains, so that only the door is level with the earth outside, the rest of the building hanging over the slope, and being supported by stout wooden poles; thus a space is obtained, which, freely admitting air, is filled with marl or other suitable material. After two or three years this material is removed, lixiviated with water, mixed with caustic lime and wood ash, and boiled down. The liquor having been sufficiently evaporated, is decanted from the sediment and left for crystallisation; the quantity of saltpetre varying from 50 to 200 lbs. for each stable.*

Treatment of the Ripe Saltpetre Earth.—The crude salt from the heaps is converted into potassium nitrate by the following processes:—*a.* The earth is lixiviated with water, this operation being known as the preparation of raw lye. *b.* The raw lye is broken, that is to say, it is mixed with a solution of a potash salt in order to convert the magnesium and calcium nitrates present into potassium nitrate. *c.* Evaporation of this liquor to obtain crude crystallised saltpetre. *d.* Refining the crude saltpetre.

Preparation of Raw Lye.—The ripe earth is lixiviated to obtain all the valuable soluble matter, it being expedient to use as little water as possible in order to save fuel in the subsequent evaporation, for which the liquor is ready when it contains from 12 to 13 per cent. of soluble salts.

Breaking up the Raw Lye.—The raw lye, sometimes known as soil water, contains the nitrates of lime, magnesia, potassa, soda, the chlorides of calcium, magnesium, and potassium; also ammoniacal salts and organic matter of vegetable as well as of animal origin. In order to convert the magnesium and calcium nitrates into potassium nitrate, the raw lye is broken up as it is termed, that is to say, there is added to it a solution of 1 part potassium carbonate in 2 parts water—

$$\left.\begin{array}{l}\text{Calcium nitrate, } Ca(NO_3)_2\\ \text{Magnesium nitrate, } Mg(NO_3)\\ \text{Potassium carbonate, } 2K_2CO_3\end{array}\right\} \text{ yield } \left\{\begin{array}{l}\text{Potassium nitrate, } 4KNO_3.\\ \text{Calcium carbonate, } CaCO_3.\\ \text{Magnesium carbonate, } MgCO_3.\end{array}\right.$$

The calcium and magnesium chlorides are also decomposed, being converted into carbonates, while potassium chloride is formed. The addition of the solution of potassa to the raw lye is continued as long as a precipitate is formed; in order, however, to have some approximative idea of the quantity of potassium carbonate which may be required a test experiment is made with ½ litre of the raw lye.

Sometimes potassium sulphate is used instead of the carbonate, but in that case the magnesia salts of the raw lye have first to be decomposed by milk of lime, an operation

* In London 100 tons of saltpetre were obtained in a similar manner in 1873.

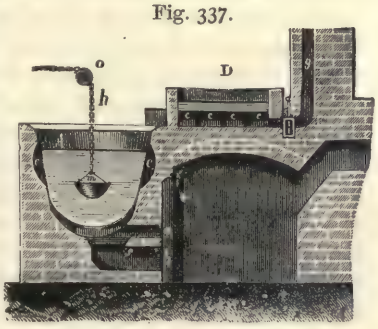
which has to be followed by the evaporation of the fluid. If, after this, potassium sulphate is added, calcium sulphate is precipitated—

$$[Ca(NO_3)_2 + K_2SO_4 = 2KNO_3 + CaSO_4].$$

When potassium chloride is used for the decomposition of raw lye, the salts of magnesia are first removed by the addition of milk of lime; and the clear supernatant fluid having been decanted from the sediment, there is added a mixture of equal molecules of potassium chloride and sodium sulphate, the result being the formation of gypsum, while the sodium nitrate generated exchanges with the potassium chloride, carrying over to the latter the nitric acid, and taking up the chlorine to form common salt.

Boiling down the Raw Lye.—The clarified raw lye decanted from the precipitate of the earthy carbonates consists of a solution in which there are present the potassium and sodium chlorides, potassium nitrate, ammonium carbonate, excess of potassium carbonate, and colouring matter. The boiling down of this liquid is effected in copper cauldrons, Fig. 337, so set in the furnace as to admit of the circulation of the hot air and smoke from the fire-place, passing by *c c* below the heating pan, and thence by *g* into the chimney. In some works this waste heat is utilised in drying the saltpetre flour. As the bulk of the fluid in the cauldron decreases by evaporation, fresh lye enters by means of a pipe and tap from the pan, D. About the third day the alkaline chlorides begin to be deposited, and the workmen have then to take great care to prevent these salts from becoming what is technically termed burnt, which might give rise to serious explosions, and for this purpose the liquid is stirred with stout wooden poles. After each stirring the loose saline matter is removed from the boiling liquid by means of perforated copper ladles. However, as a hard deposit is always formed, a peculiar arrangement exhibited in Fig. 337, consisting of a shallow vessel, *m*, suspended by a chain, *h*, and weighted with a piece of stone, is lowered into the middle of the cauldron to about 6 centimetres from the bottom, the object being to catch the solid particles, which would, when aggregating, form an incrustation, previously to their reaching the bottom of the vessel; and as no ebullition takes place at *m*, the particles once deposited remain there, and can be readily removed by raising the dish out of the cauldron, and emptying it into a box placed over the cauldron, the bottom of the box being perforated to admit of any liquor which may have been raised with the solid salt to return again to the cauldron. The deposit thus removed consists chiefly of gypsum and carbonate of lime.

Fig. 337.



When a portion of the impurities contained in the boiling liquid have been removed, the raw lye still frequently contains some sodium chloride, as this salt is not, as is the case with nitre, more soluble in boiling than in cold water. The abundant crystallisation of the saltpetre is a sign that the lye has been sufficiently evaporated; in order, however, to prove this, a small sample is taken, and if on cooling the nitre crystallises so that the greater part of the sample becomes a solid mass, the liquid is run into tanks and left for 5 or 6 hours, during which time impurities are deposited, and the liquid rendered quite clear. As soon as the temperature of the liquid has fallen to 60°, it is poured into copper crystallisation vessels; after a lapse of 24 hours the crystallisation is complete, and the mother-liquor being separated from the salt is employed in a subsequent operation.

Refining the Crude Saltpetre.—The crude saltpetre is yellow-coloured, and contains on an average some 20 per cent. of impurities, consisting of deliquescent chlorides,

earthy salts, and water. The object to be attained by the refining is the removal of these substances. At the present day a large portion of the refined saltpetre met with in commerce is obtained by the refining of the crude saltpetre imported from India. It may be noted that this importation is steadily increasing, there being, in 1860, 16,460,300 kilos., and in 1868, 33,062,000 kilos. of the salt brought to England; and, indeed, the production of saltpetre from natural sources in Europe is now limited to very few and unimportant localities.

The method of refining saltpetre is based upon the fact that potassium nitrate is far more soluble in hot water than are the sodium and potassium chlorides. 600 litres of water are poured into a large cauldron, and 24 cwts. of the crude saltpetre are added at a gradually increasing temperature; as soon as the solution boils, 36 cwts. more crude saltpetre are added. Supposing the crude nitre to contain 20 per cent. of alkaline chlorides, the whole of the nitre will be dissolved in this quantity of water, while a portion of the chlorides will remain undissolved even at the boiling-point. The non-dissolved salt is removed by a perforated ladle, and the scum rising to the surface of the boiling liquid by the aid of a flat strainer. The organic matter present in the solution is removed by the aid of a solution of glue—from 20 to 50 grammes of glue dissolved in 2 litres of water are taken for each hundredweight of saltpetre. In order that the saltpetre may crystallise, the quantity of water is increased to 1000 litres, and as soon as this water is added the organic matter entangled in the glue rises as a scum to the surface and is removed. The operation having progressed so far, and the liquid being rendered quite clear, it is kept at a temperature of 88° for about twelve hours, and then carefully ladled into copper crystallising vessels, constructed with the bottom a little higher at one end than at the other. The solution would yield on cooling large crystals of saltpetre, but this is purposely prevented by keeping the liquid in motion by means of stirrers, so as to produce the so-called flour of saltpetre, which is really the salt in a finely divided state. This is next transferred to wooden boxes, termed wash-vessels, 10 feet long by 4 feet wide, provided with a double bottom, the inner one being perforated; between the two bottoms holes are bored through the sides of the vessel, and when not required plugged with wooden pegs. Over the flour of saltpetre contained in these wooden troughs, 60 lbs. of a very concentrated solution of pure potassium nitrate are poured, and allowed to remain for two to three hours, the plugs being left in the holes. The plugs are then removed, the liquor run off, the holes again plugged, and the operation twice repeated, first with a fresh 60 lbs., and next with 24 lbs. of the solution of potassium nitrate, followed in each case by an equal quantity of cold water. The liquors which are run off in these operations are of course collected, the first being added to the crude saltpetre solution, while the latter, being solutions of nearly pure nitre, are again employed. The saltpetre is next dried at a gentle heat in a shallow vessel, sifted, and packed in casks.

Preparation of Potassium Nitrate from Chili Saltpetre.—During the last twenty years the preparation of potassium nitrate from Chili saltpetre has become an important branch of manufacturing industry. The product obtained by any of the following processes is called "converted saltpetre," to distinguish it from the preceding preparation. The method of procedure may be one of the following:—

1. The sodium nitrate is decomposed by means of potassium chloride—

100 kilos. of sodium nitrate 87·9 kilos. of potassium chloride	} yield {	119·1 kilos. potassium nitrate. 68·8 kilos. common salt.

MM. Longchamp, Anthon, and Kuhlmann first suggested this mode of preparation, which is now generally used on the large scale, as the decomposition of both salts is very complete, and as the common salt as well as the saltpetre can be utilised. The potassium chloride is obtained by the decomposition of carnallite, or by means already mentioned.

Equivalent quantities of sodium nitrate and of chloride of potassium are dissolved in water contained in a cauldron of some 4000 litres cubic capacity. As the nitrate of soda of commerce (Chili saltpetre) does not, as regards purity, vary very much from 96 per cent., some 7 cwts. are usually taken, while of the chloride of potassium, which varies in purity from 60 to 90 per cent., a quantity is taken corresponding, as regards the amount of pure chloride, to the quantity of sodium nitrate. The chloride of potassium is first dissolved, the hot solution being brought to a sp. gr. = 1·2 to 1·21; next the sodium nitrate is added, and the liquid brought, while constantly heated, to a sp. gr. = 1·5. The sodium chloride continuously deposited is removed by perforated ladles, and placed on a sloping plank so that the mother-liquor may flow back into the cauldron, care being taken to wash this salt afterwards, so as to remove all potassium nitrate, the washings being poured back into the cauldron. When the liquid in the cauldron has been brought to 1·5 sp. gr.—an aqueous solution of potassium nitrate at 15°, with a sp. gr. = 1·144, contains 21·074 per cent. of that salt—the fire is extinguished, the liquid left to clear, the common salt still present carrying down all impurities, and when clear it is ladled into very shallow crystallising vessels, where the crystallisation is finished in twenty-four hours. The mother-liquor having been run off, the crystals are thoroughly drained and covered with water, which is left in contact with the salt for some seven to eight hours, and then run off; this operation is repeated during the next day; the mother-liquor and washings are poured back into the cauldron at a subsequent operation.

2. Sodium nitrate is first converted into sodium chloride by means of barium chloride, barium nitrate being formed, and in its turn converted into potassium nitrate by the aid of potassium sulphate:—

a. 85 kilos. of sodium nitrate, 122 kilos. of barium chloride } yield { 130·5 kilos. barium nitrate. 58·5 kilos. of common salt.

β. 130·5 kilos. of barium nitrate require for conversion into potassium nitrate } 87·2 kilos. of potassium sulphate, or 69·2 kilos. of potassium carbonate.

When potassium sulphate is used, permanent-white, baryta-white, or barium sulphate is obtained as a by-product, while if potassium carbonate is used, barium carbonate remains, and of course may be readily re-converted into barium chloride. In order to estimate the advantages of either process, the following points must be kept in view:—*a.* Taking into consideration that it is profitable to convert native barium carbonate into barium chloride—for instance, by exposing witherite to the hydrochloric acid fumes produced in alkali works by the decomposition of salt—and to precipitate an aqueous solution with dilute sulphuric acid to obtain permanent-white, it may be inferred that it will also pay to obtain it as a by-product. *b.* Notwithstanding the complication of this process, it is advantageous as producing a far purer potassium nitrate.

3. Sodium nitrate is converted by means of potash into the nitrate of that base, pure soda being obtained as a by-product:—

85 kilos. Chili saltpetre, 69·2 kilos. potassium carbonate } yield { 101·2 kilos. of potassium nitrate. 53 kilos. of soda (calcined).

This mode of manufacturing saltpetre was first introduced into Germany during the Crimean War (1854–55) by M. Wöllner, of Cologne, who established large works to prepare saltpetre in this way, and very soon after, during the continuance of the war, five other manufactories of potash saltpetre had been established on this method. In 1862 the production amounted to 7,500,000 lbs. of potash saltpetre, the potassium carbonate required being obtained from beet-root molasses, the soda resulting as a by-product being even superior to that produced by Leblanc's process.

According to M. Lunge's description, this process, first suggested by MM. Landmann and Gentele, afterwards modified by M. Schnitzer, and practically applied by M. Nöllner, is carried on in Lancashire in the following manner:—There is added to a caustic potash lye of 1·5 sp. gr., containing about 50 per cent. of dry caustic potassa, an equivalent quantity of sodium nitrate, and the whole, after a short time, is crystallised. The potassium nitrate having been separated from the mother-liquor, that fluid, the density of which has been greatly decreased by the reaction, is by evaporation again brought to its former density, and yields on cooling another crop of crystals of potash-saltpetre. Usually there then only remains a solution containing caustic soda with saline impurities; sometimes, however, a third crop of crystals is obtained. The deposit during the evaporation is chiefly sodium carbonate derived from the sodium chloride contained in the potassium chloride from which the caustic potassa is made, this chloride being also converted into carbonate. The small quantities of undecomposed potassium and sodium chlorides and calcium sulphate are retained in the mother-liquor, which is evaporated to dryness and ignited, yielding a dry caustic soda of a bluish-colour. The crystallised potassium nitrate is now carefully refined to remove all impurities to about 0·1 per cent. of sodium chloride, converted into saltpetre-flour, and treated as already described. Notwithstanding that the various operations have been carried on in iron vessels, the salt does not contain any of this metal, nor is the colour in any way affected. The flour is dried in a room 2 metres wide by 5 metres in length, built of brick-work, similarly to the chloride of lime rooms, and having a pointed arched roof 2 metres in height. The saltpetre-flour is spread on a wooden floor, under which extends a series of hot-air pipes, keeping the temperature at 70°, and very rapidly effecting the drying.

Testing the Saltpetre.—If, when perfectly pure, saltpetre is carefully fused and allowed to cool, it becomes a white mass, exhibiting a coarsely radiated fracture; even so small a quantity as $\frac{1}{80}$th of sodium chloride causes the fracture to appear somewhat granular; with $\frac{1}{40}$th the centre is not at all radiated, and is less transparent; and with $\frac{1}{30}$th the radiation is only slightly perceptible at the edges of the fracture. Sodium nitrate has the same effect. This method of testing the purity of nitre, due to M. Schwartz, is employed in Sweden, where every landowner pays a portion of his taxes in saltpetre of a specified degree of purity. A great number of methods of testing saltpetre have been suggested by various authors for the purposes of the manufacture of gunpowder, not, however, in sufficiently general use to interest the reader. Werther's test for chlorine and sulphuric acid is by solutions of the barium and silver nitrates; the silver solution is such that each division of the burette corresponds to 0·004 grammes of chlorine, and the baryta solution to 0·002 gramme of sulphuric acid. According to Reich's plan, 0·5 gramme of dried and pulverised saltpetre is ignited to a dull red heat, with from 4 to 6 times its weight of pulverised quartz; the nitric acid is expelled, the loss of weight consequently indicating the quantity, the sulphates and chlorides not being decomposed at a dull red heat. If the loss $= d$, we have 1·874 d potassium nitrate, or 1·574 d sodium nitrate.

Another method, due to Dr. A. Wagner, is based upon the fact that when saltpetre, or any other nitrate, is ignited, access of air being excluded, with an excess of chromic oxide and sodium carbonate, the nitric acid oxidises the chromic oxide according to the formula $Cr_2O_3 + NO_5 = 2CrO_3 + NO_2$. 76·4 parts, by weight, of chromic oxide are oxidised to chromic acid by 54 parts of nitric acid, or 1 of chromic oxide by 0·7068 of nitric acid. The operation is performed by taking from 0.3 to 0·4 gramme of the nitrate, mixing it intimately with 3 grammes of chromic oxide and 1 gramme of sodium carbonate, introducing this mixture into a hard German glass combustion-tube, one end of which is drawn out, and a vulcanised india-rubber tube attached to it, which is made to dip for about a quarter of an inch into water, while to

the other open end, by means of a cork and glass tube bent at right angles, an apparatus is fitted for the evolution of carbonic acid gas, which is made to pass through the tube before igniting it, and kept passing through all the time until the tube is quite cool again after ignition. The contents of the tube are placed in warm water, and after filtration the chromic acid is estimated by Rose's method. This process of estimating nitric acid has been found to yield very accurate results.

Uses of Saltpetre.—This salt is employed for many purposes, the most important being (1) The manufacture of gunpowder. (2) The manufacture of sulphuric and nitric acids. (3) Glass-making, to refine the *metal* as it is termed. (4) As oxidant and flux in many metallurgical operations. By the ignition of 1 part of nitre and 2 of argol, in some cases refined argol (cream of tartar), *black flux* is formed consisting of an intimate mixture of potassium carbonate and finely divided charcoal. The ignition of equal parts of saltpetre and cream of tartar gives *white flux*, consisting of a mixture of potassium carbonate and undecomposed saltpetre; both these mixtures are often used. Black flux may also be made by intimately mixing potassium carbonate with lamp-black and white flux. (5) When mixed with common salt and sugar in the salting and curing of meat. (6) For preparing fluxing and detonating powders. Baumé's fluxing powder is a mixture of 3 parts of nitre, 1 of pulverised sulphur, and 1 of sawdust from resinous wood; if some of this mixture be placed with a small copper or silver coin in a nutshell and ignited, the coin is melted in consequence of the formation of a readily fusible metallic sulphide, while the nutshell is not injured. Detonating powder is a mixture of 3 parts saltpetre, 2 potassium carbonate, and 1 pulverised sulphur; this powder when placed on a piece of sheet-iron, and heated over a lamp, will explode with a loud report, yielding a large volume of gas:

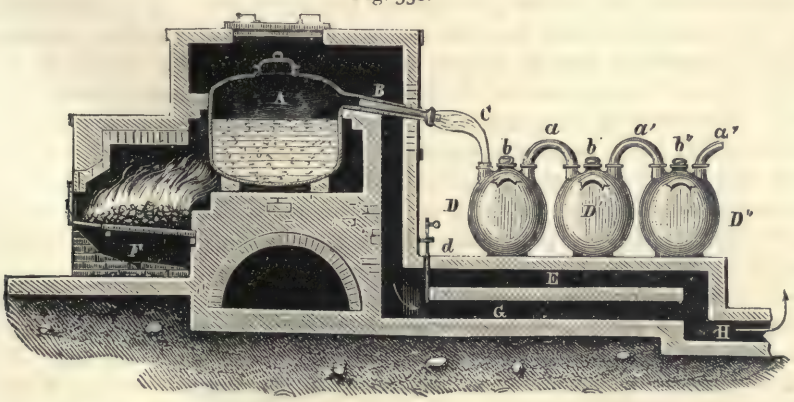
$$\left.\begin{array}{l}\text{Saltpetre, } 6KNO_3,\\ \text{Potassium carbonate, } 2K_2CO_3,\\ \text{Sulphur, } 5S.\end{array}\right\} = \left\{\begin{array}{l}\text{Nitrogen, } 6N.\\ \text{Carbonic acid, } 2CO_2.\\ \text{Potassium sulphate, } 5K_2SO_4.\end{array}\right.$$

(7) For manure in agriculture. (8) In many pharmaceutical preparations. (9) For the preparation of Heaton steel.

NITRIC ACID.

Methods of Manufacturing Nitric Acid.—This acid (NHO_3) is generally manufactured by decomposing nitrate of soda by sulphuric acid, and condensing the vapours set free. It is obtained on the large scale by placing in a cast-iron vessel, *A*, Fig. 338, the nitrate to be operated upon, to which is added by means of a funnel strong sulphuric

Fig. 338.



acid. The lid is replaced, and the vessel connected by means of the clay-lined tube, *B*, with the glass tube, *C*, dipping into the large stoneware flask, *D*, which serves the purpose

of a receiver. This flask is connected by means of a tube, *a*, to a similar vessel, *D'*, and that to a third vessel, *D''*, and so on, in order to completely condense the vapours which might have escaped through the first, second, and third vessels. The iron vessel, *A*, is heated by means of the fire placed in the hearth, *F*, the smoke and hot gases being carried off by *G H*. At the outset of the operation the damper, *d*, is so regulated as to shut off the lower channel, and cause the smoke and hot gases to pass through *E*, heating the vessels *D*, *D'*, and *D''*, this precaution being required to prevent their cracking by the hot acid vapours entering from *A*. As soon, however, as the distillation has fairly commenced, the damper is altered to shut off *E*, and pass the hot air and gases through *G*. The nitric acid condensed in the first receiver is sufficiently strong for immediate use, but to facilitate the condensation some water has been poured through the openings, *b' b''*, into the other receivers, the acid from which is weaker and known in the trade as aquafortis.

Very frequently the distillation of nitric acid is conducted in a series of glass retorts placed on a sand-bath; there are generally two rows of retorts, the heating apparatus being a galley oven. If the acid is to be pure, the first condensations are collected in separate receivers, as the acid first condensed contains hydrochloric acid due to the chlorides contained in the nitrates under operation.

The proportion of materials employed is—

30 kilos. of potassium nitrate to 29 kilos. of strong sulphuric acid; or,

17 „ sodium nitrate to 14·5 „ „ „ „

The sodium bisulphate which remains may either be used for the preparation of fuming sulphuric acid, or may be mixed with common salt, and ignited, to produce hydrochloric acid and neutral sodium sulphate, available in the preparation of sodium carbonate.

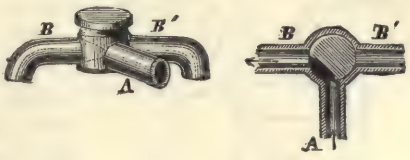
The nitric acid (NHO_3) resulting from the above operation is a colourless, transparent fluid, having a sp. gr. of 1·55, and boiling at 80°. When diluted with water the boiling-point is higher. An acid containing 100 parts (NHO_3) and 50 parts of water boils at 129°, but if the dilution with water is carried further the boiling-point is again lowered; consequently when such an acid is heated above 100° the result is that at first water with only a trace of acid distils over, and if the process be continued the boiling-point gradually increases until it reaches 130°, when there distils over what is termed double aquafortis, sp. gr. = 1·35 to 1·45, ordinary or single aquafortis having a sp. gr. = 1·19 to 1·25. Nitric acid, when in contact with air, emits fumes, owing to the absorption of water from the atmosphere.

Bleaching Nitric Acid.—The stronger acid manufactured as described is usually of a yellow colour, due to the presence of hyponitric acid. If a colourless acid is desired, the crude acid must be submitted to a bleaching operation, conducted as follows:—The coloured acid is poured into large glass vessels placed in a water-bath, heated to 80° to 90°, and left in these vessels as long as any coloured vapours are given off. The escaping hyponitric acid is carried by means of glass or glazed earthenware tubes either into a sulphuric acid chamber and there utilised, or into the flue of a chimney, and thus into the air. Any hydrochloric acid present in the nitric acid is also carried off as chlorine. In order to remove any sulphuric acid it is necessary to distil the nitric acid over pure barium nitrate, while the last traces of hydrochloric acid can be removed by distillation over pure silver nitrate.

Condensation of the Nitric Acid.—More recently improvements have been made in the manufacture of nitric acid, bearing especially upon the possibility of omitting the bleaching process, and a better mode of condensing the vapours of the acid. The first point is supplied by an arrangement introduced in the manufactory of M. Chevé, in Paris. Every practical chemist knows that the red vapours appear only at the outset and towards the end of the distillation of the nitric acid, and it is therefore only

required to distil fractionally to obtain on the one hand a red-coloured acid, the *acidum nitroso-nitricum* or *acidum nitricum fumans fortissime* of the pharmaceutists, and on the other a colourless acid, which can be forthwith delivered to the consumer. In order to practically effect the fractional distillation, a tap of porcelain or hard-fired stoneware, constructed as exhibited in Fig. 339, is fixed by means of *A*, in communication with the iron distilling vessel, while the tubes *B* and *B'* are connected with two different receivers. The tap is bored in such a manner, that at pleasure either the communication between *A* and *B'*, or the communication between *A* and *B*, can be established. By proper management, therefore, it is possible to separate the red-coloured acid entirely and without any additional expense, from the colourless acid.*

Fig. 339.



For preparing a *chemically pure nitric acid* it is best to distil the tetra-hydrated acid (sp. gr. 1·42. = 84° Tw.) in glass vessels and receive the product which goes over separately as long as it occasions a turbidity with a solution of silver nitrate. The receiver is then changed and the rest of the acid distilled off down to a small residue. At some works a purified nitre is used for obtaining nitric acid free from chlorine.

Instead of the apparatus figured, horizontal cylinders of cast iron are employed as stills, fixed so that they are uniformly encompassed by the hot gases. The acid going over last should be collected separately as the iron is attacked when the cylinder has cooled down. The two ends of the cylinder are not exposed to the fire and are best closed with plates of sandstone, cemented in with a mixture of iron filings, sal ammoniac, sulphur and vinegar. This cement dries quickly and resists the action of heat and acid. The front plate has in its upper half an opening for introducing the nitre. This opening can be closed by a stone plug, luted in with clay. In this plug there is a small hole through which the sulphuric acid is introduced. The gases which escape are collected in the usual way by passage through a scrubber. The proportion of sulphuric acid to nitre is not uniform. Some makers use to 1 mol. nitre $1\frac{3}{4}$ mol. sulphuric acid, in which case the bisulphate formed so reduces the melting-point of the residue of sulphate that it may be run out at the end of the operation.

The strength of the sulphuric acid depends on that of the nitric acid to be produced. In most cases an acid is taken of 1·718 sp. gr. (= 143° Tw.) The mixture froths then least, so that the retorts or cylinders can be filled up rather high. The mean strength of the nitric acid thus obtained ranges from 1·38 to 1·41 sp. gr. (76° to 82° Tw.). For nitric acid at 1·50 to 1·52 sp. gr. dried nitre is employed and sulphuric acid of sp. gr. 1·85 (= 170° Tw.).

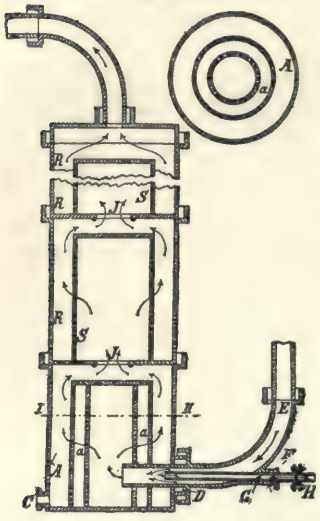
The bisulphate remaining serves either for producing fuming sulphuric acid and anhydride or it is ignited with common salt to yield salt-cake and hydrochloric acid.

Nitric acid may be produced by the action of manganous chloride upon sodium nitrate. If a mixture of both salts is heated to 230° there are evolved nitrous fumes ($NO_2 + O$), and there remains a manganese oxide ($Mn_3O_8 = 2MnO + 3MnO_2$) which may serve for the production of chlorine.

* Coloured nitric acids are sometimes decolorised by the addition of a small quantity of lead peroxide, which gives off oxygen to the lower nitrogen oxides, and is at the same time converted into lead nitrate, which is almost insoluble in nitric acid. A so-called "single aquafortis" supplied to dyers has to be very carefully purified from sulphuric acid and the lower nitrogen oxides, but may contain a certain proportion of hydrochloric acid or of ammonium chloride.

If the mixture of NO_2 and O is passed into a condensation apparatus along with water it is converted into nitric acid, the excess of the hyponitric acid being resolved into nitric acid and nitric oxide. If the air in the apparatus is sufficient to convert the entire nitric oxide into nitric acid the process is repeated. From numerous experiments in clay retorts, conducted by Kuhlmann, he found on this process 100 parts nitre yielded a mean of 125 to 126 nitric acid at 60° Tw., the yield in the ordinary process being 127–128 per cent. A similar result was obtained with chlorides, especially calcium and magnesium chlorides. The sulphates also, even those which are very permanent and do not in any wise play the part of an acid, effect the decomposition of the alkaline nitrates.

Fig. 340.



For obtaining nitric acid by the oxidation and condensation of the lower oxides of nitrogen, Rohrmann (Fig. 340) uses an earthen condensing columm. The lower part, *A*, contains a perforated inverted beaker, *a*. At the foot is the efflux pipe, *C*, and on the other side the outflow, *D*, which receives the junction-pipe, *E*, through which is led nitric oxide gas obtained in any manner. To the pipe, *E*, is affixed the piece, *F*, through which there enters a pipe, *G*, which at its upper end receives the blast, *H*, for the introduction of steam and air. Above the beaker, *A*, rise the beakers, *R*, in the form of a column. They have a large aperture, *J*, at the bottom, with a thickened margin at the under side. Over the opening, *J*, is the inverted beaker, *S*, the side of which is perforated like a sieve. In the earthen pipe-connections placed between the several columns, there is introduced a lantern provided with glass discs. The openings for the access of air in the blast can be altered.

The Densities of Nitric Acid.—According to J. Kolb, the connection between the sp. gr. of nitric acid and its per centage of concentrated acid is as follows:—

100 parts contain		Density.		100 parts contain		Density.	
NHO_3.	N_2O_5.	At 0°.	At 15°C.	NHO_3.	N_2O_5.	At 0°.	At 15° C.
100·00	85·71	1·559	1·530	50·99	43·70	1·341	1·323
97·00	83·14	1·548	1·520	45·00	38·57	1·300	1·284
94·00	80·57	1·537	1·509	40·00	34·28	1·267	1·251
92·00	78·85	1·529	1·503	33·86	29·02	1·226	1·211
91·00	78·00	1·526	1·499	30·00	25·71	1·200	1·185
90·00	77·15	1·522	1·495	25·71	22·04	1·171	1·157
85·00	72·86	1·503	1·478	23·00	19·71	1·153	1·138
80·00	68·57	1·484	1·460	20·00	17·14	1·132	1·120
75·00	64·28	1·465	1·442	15·00	12·85	1·099	1·089
69·96	60·00	1·444	1·423	11·41	9·77	1·075	1·067
65·07	55·77	1·420	1·400	4·00	3·42	1·026	1·022
60·00	51·43	1·393	1·374	2·00	1·71	1·013	1·010
55·00	47·14	1·365	1·346				

The following table exhibits comparative data of density and degrees according to Beaumé:—

Degrees according to Beaumé.	Density.	100 parts contain at 0°		100 parts contain at 15° C.	
		NHO_3.	N_2O_5.	NHO_3.	N_2O_5.
6	1·044	6·7	5·7	7·6	6·5
7	1·052	8·0	6·9	9·0	7·7
9	1·067	10·2	8·7	11·4	9·8
10	1·075	11·4	9·8	12·7	10·9
15	1·116	17·6	15·1	19·4	16·6
20	1·161	24·2	20·7	26·3	22·5
25	1·210	31·4	26·9	33·8	28·9
30	1·261	39·1	33·5	41·5	35·6
35	1·321	48·0	41·1	50·7	43·5
40	1·384	58·4	50·0	61·7	52·9
45	1·454	72·2	61·9	78·4	72·2
46	1·470	76·1	65·2	83·0	71·1
47	1·485	80·2	68·7	87·1	74·7

47°	B. correspond to	96°	Twaddell.	34°	B. correspond to	60°	Twaddell.
46°	"	92°	"	29°	"	50°	"
45°	"	88°	"	25°	"	40°	"
43°	"	84°	"	20°	"	30°	"
42°	"	80°	"	14°	"	20°	"
38°	"	70°	"	7°	"	10°	"

Nitric acid of	1·52	sp. gr. boils at	86°	Nitric acid of	1·35	sp. gr. boils at	117°
"	1·50	"	99°	"	1·30	"	113°
"	1·45	"	115°	"	1·20	"	108°
"	1·42	"	123°	"	1·15	"	104°
"	1·40	"	119°				

Fuming nitric acid is generally now obtained by mixing in a retort 100 parts of nitre with 3·5 parts of starch and adding 100 parts of sulphuric acid at sp. gr. 1·85. The retort should only be filled to one-third.

Fuming nitric acid or even nitric acid of sp. gr. 1·26, if it comes in contact with dry packing materials, may give rise to fires. Straw, or the like, should therefore be previously steeped in a solution (saturated in the cold) of Glauber's salt, Epsoms—*i.e.*, magnesium sulphate, &c.

Technical Applications of Nitric Acid.—The technical application of nitric acid is based on its property of oxidation when in contact with certain substances, the acid splitting up into nitrogen dioxide, hyponitric acid and ozone, the latter forming with the body which caused the decomposition of the acid either an oxide or a peculiar compound, while the hyponitric acid, when organic substances are present capable of combining with it, forms the nitro-compounds, nitrobenzole, nitronaphthaline, nitroglycerine, nitromannite, nitrocellulose, or gun-cotton, &c. A large number of metals are soluble in moderately concentrated nitric acid, but the strongest acid fails to act upon iron and lead. Proteine compounds, albumen, the skin of the hands, silk, horn, feathers, &c., are stained yellow by nitric acid, hence the use of this acid in dyeing silk. If the acid is in contact with these substances for any length of time, they are completely decomposed, and partly converted into picric acid. Starch, cellulose, and sugar, are converted by the action of nitric acid into oxalic acid; but very dilute nitric acid converts starch into dextrine, and concentrated acid into xyloidine. Owing to the property nitric acid possesses of destroying certain pigments—for instance, indigo—it is sometimes employed in calico printing to produce a yellow pattern on an indigo ground. This acid is also used in dyeing woollen materials; in hat-making, to prepare a mercurial solution used in dressing felt hats; in the manufacture of sulphuric acid; in the preparation of lacquers; in the preparation of nitrate of iron, a mordant used in dyeing silk and cotton black; for preparing picric acid from carbolic acid, and naphthaline-yellow from naphthaline; in the manufacture of nitrobenzol, nitrotoluol, and

phthalic acid; and for the preparation of nitrate of silver, arsenic acid, fulminating mercury, nitroglycerine, dynamite, &c.

It serves further, under the name *Rouille*, for producing a compound of iron fraudulently used for "loading" or "weighting" black silks in the process of dyeing, of which ten tons are consumed daily in Lyons.

EXPLOSIVES.

Gunpowder.—The substance known as gunpowder, or simply as powder, is a more or less finely granulated mechanical mixture of saltpetre, sulphur, and charcoal, the quantities of these materials being properly defined. It ignites at 300°, also when touched with a red-hot or burning body, or under certain conditions by friction or a sudden blow. Powder under these conditions burns off rapidly but not instantaneously, yielding as the products of its combustion nitrogen, carbonic acid, or carbonic oxide, while there remains a solid substance consisting of a mixture of potassium sulphate and carbonate. When the powder is ignited in a closed vessel, the sudden evolution of the large volume of gases causes a pressure almost impossible to be withstood; and even in guns and large ordnance, in which one side of the vessel is formed by the yielding shot, the metal forming the other sides must possess great strength and elasticity. In guns and artillery the pressure only lasts as long as the ball is inside the gun, therefore the slower the combustion of the powder through its entire mass, the lower is the velocity of the projectile.

Manufacture of Gunpowder.—It is essential that the materials employed in the manufacture of powder should be very pure; the saltpetre should not contain any chlorides; the sulphur should be free from sulphurous acid, hence not flowers of sulphur but refined roll sulphur is used; and lastly the charcoal requires very great attention. The wood from which it is intended to prepare a charcoal for gunpowder should be such as yields the least possible quantity of ash, while the charcoal should be soft, like that used in pharmacy. The stems of the hemp and flax plants, especially the former, yield excellent charcoal, but in consequence of the limited supply, the wood of the wild plum tree (*Prunus padus*) is largely used in Germany, France, and Belgium; and in England the lime, willow, poplar, horse-chestnut, hazel, cherry, alder, and other light white woods are employed for this purpose. All these varieties yield on being carbonised—effected in various ways, in retorts similar to those used in gas-works, in pits dug in the earth, or by the aid of superheated steam, the wood being placed in boilers, &c.—from 35 to 40 per cent. charcoal. The temperature during the progess of carbonisation being kept as low as possible, there is obtained a very soft reddish-brown charcoal, known as *charbon roux*. The charcoal prepared in cylindrically shaped retorts is very inappropiately designated distilled charcoal.

Mechanical Operations of Powder Manufacture.—These operations include:—

1. The pulverising of the ingredients. 2. The intimate mixing of these substances. 3. The moistening of the mixture. 4. The caking or pressing. 5. The granulation and sorting of the grain, as it is termed. 6. Surfacing the powder. 7. Drying. 8. Sifting from the dust.

Pulverising the Ingredients.—This operation can be performed in three different ways:—

a By means of revolving drums.
b. By mill stones; or
c. In stamping-mills.

a. The pulverisation by means of revolving drums is an invention due to the French Revolution, and has the advantages of being very effective, rapid in execution, and of preventing the flying about of the ingredients in a fine dust. The drums are made of

wood, lined with stout leather, and provided with a series of projections. The substance to be pulverised is put into the drum with a number of bronze balls of about $\frac{1}{4}$ inch diameter, their action aided by that of the projections, when the drum is turned on its horizontal axis at a moderate speed, soon effecting a reduction to a fine powder. The charcoal and sulphur are separately pulverised; the saltpetre being obtained as a flour. (*See* Saltpetre.)

b. Grinding by the aid of mill-stones. Two heavy vertical stones, similar to those in use for crushing linseed, revolve on a fixed horizontal stone. This contrivance is the most frequently used.

a. Stampers are now employed only in small powder-mills. Frequently 10 to 12 stamps made of hard wood are placed in a row, each stamp being fitted with a bronze shoe, the entire weight being about 1 cwt. The stamps are moved by machinery, and make from 40 to 60 beats a minute. The materials to be pulverised are placed in mortar-shaped cavities in a solid block of oak wood, each cavity containing 16 to 20 lbs. In Switzerland hammers instead of the stampers are employed.

Mixing the Ingredients.—The mixing is performed by the aid of drums similar in size and shape to those used in the pulverisation, but made of stout leather instead of wood. The mixing of 100 kilos. of the ingredients, aided by the action of 150 bronze balls, takes fully three hours, the drum making ten revolutions a minute. It is usual to moisten the materials with 1 to 2 per cent. of water, supplied by fine jets regulated by taps.

When stampers and mill-work are employed, the sulphur and charcoal are first separately pulverised by 1000 blows, and saltpetre having been mixed with these ingredients in the proper proportion, the machinery is again set in motion, and at first, after every 2000 blows, and then after every 4000 blows, the contents of the stamp-holes are removed from the one to the other, this operation being repeated some six or eight times. Where drums are used for the mixing operation, the moistening takes place after the mixture has been removed to a wooden trough, where 8 to 10 per cent. of its weight of water is added, care being taken to stir with a wooden spatula.

Caking or Pressing the Powder.—This operation, which in stamping-mills is the last of a continuous series, is separately performed where other machinery is employed. In the French and German powder-mills, the compression is effected in a rolling-mill, the rollers having a diameter of 0·6 metre. The lower roller is made of wood, the upper of bronze; between the two an endless piece of stout linen is arranged, and upon this the moist powder is placed. The cakes are 1 to 2 centimetres in thickness with the hardness and very much the appearance of clay-slate.

The operation of pressing is of great importance; the stronger the pressure the greater the quantity of active material present in a given bulk, and hence the larger the volume of gas given off by the ignition of the powder. In many English powder-mills the pressing is effected by very powerful hydraulic machines, because, within certain limits, the more the materials are pressed, the more slowly the powder burns when finished, while the temperature of ignition being lower, the expansion of the gases is less. If the powder were finished either without having undergone any pressure at all, or with only a slight pressure, it would act as a detonating-powder, the decomposition being instantaneous throughout its entire mass.

Granulation of the Cake, and Sorting the Powder.—The conversion of the cake into granules is effected—

1. By means of sieves.
2. By means of peculiarly constructed rollers, Congreve's method; or
3. According to Champy's method.

The granulation of gunpowder by the aid of sieves is carried on in the following manner:—The sieves consist of a circular wooden frame, across which a piece of parch-

ment is stretched perforated with holes; the sieves are named according to their uses, and by the size of these holes; that employed for breaking up the cake having larger holes, and bearing a name different from the sieves used to produce the granules this sieve again being distinguished from that employed for sorting the powder into the variously sized grains as commercially known. The sieves are provided with a so-called rummer, a lens-shaped disc made of hard wood, guaiacum, box, or oak-wood, motion being imparted to the sieves by hand if they are small, or by suitably arranged machinery if they are large, in which case Lefebvre's granulating-machine fitted with eight sieves in an octagonal wooden frame is generally employed.

Congreve's granulating-machine consists of three pairs of brass rollers, 0·65 metre in diameter, provided with diamond-shaped projections 2 millimetres high, the projections of the upper rollers being coarser than those of the others. The broken-up cake is conveyed to the upper rollers by means of an endless canvas sheet. The mode of feeding this sheet is somewhat peculiar and ingenious: the loose bottom of a square box filled with coarsely pounded cake is made to rise slowly upwards, and discharge the cake uniformly upon the sheet through an opening in the side of the box. The cake while passing through the rollers is granulated, and then showered upon two sets of wire-gauze sieves to which a to-and-fro motion is imparted. Below these sieves again is a frame containing wire-gauze, the meshes of which are too small to admit of the passage of ordnance powder, while the dust and cartridge-powder readily fall through upon another wire-gauze, the meshes of which retain the rifle-powder but let the dust pass. The quantity of dust made by the Congreve machine is very small, owing to the fact that the rollers do not crush but break the cake. Champy's method, by which a very round-grained powder is obtained, is performed in the following manner:—Through the hollow axis of a wooden drum a copper tube, perforated with very small holes, is carried, and from these holes water sprouts in a fine spray upon the broken-up powder-cake placed in the drum, to which a comparatively rapid motion is imparted. Each drop of water forms the nucleus of a grain of powder, which is constantly increasing in size by being turned round in the midst of a mass of damp powder-cake; the rotation of the drum is discontinued as soon as the grain has attained a sufficient size. The powder thus obtained is almost perfectly globular, but not of the same size; the sorting is effected by means of sieves, the over-sized grains being returned to the drum, as well as the under-sized grains, which become the nuclei of proper-sized grain. According to the Berne method, round-grained powder is prepared by causing the angular-shaped powder to be rotated in stout linen-bags; but by this plan much dust is formed.

Polishing the Granulated Powder.—The aim of this operation is to impart symmetry to the grain, and to separate all the dust. It is performed in drums similar to those described above; 5 cwts. of the powder is polished at a time, the drums rotating slowly for a few hours.

In some countries the polishing is effected by placing the powder in casks internally provided with quadrangular rods. In Holland, Dr. Wagner states that some black-lead is added to the powder during this operation to prevent ignition, but this is not generally done. Highly-polished powder does not readily attract moisture, and is to be preferred in a very damp climate.

Drying the Powder.—It is clear that this operation requires very great care in more than one respect. In small powder-works the powder is sometimes dried by exposure to the heat of the sun, being spread out on canvas sheets stretched in wooden frames; or the drying-room is heated by a stove. In large powder-mills other methods of drying the powder are general.

The quality of the powder very much depends on the care bestowed upon the drying. A too rapid drying entails the following disadvantages: *a.* The powder may

be very wet and not polished; coarse ordnance and ordinary military powder is never polished, and hence blackens the hands; while, although the water is driven off, the nitre is carried to the surface of the grain, which thereby cakes together. *b.* By the too rapid evaporation of the water, channels and cracks are made in the grain, impairing its density, increasing its bulk, and rendering it more hygroscopic. *c.* Lastly, rapid drying entails a large amount of dust. For these reasons gunpowder, before being placed in the drying-rooms, is exposed for some time to a gentle heat in a well-ventilated room, the heat from a waste steam-pipe being sufficient.

Sifting the Dust from the Powder.—Having been dried, the powder is sometimes glazed, as it is termed; that is to say, again polished in the manner above described; but generally this second polishing is dispensed with, and the dry powder cleansed from the dust which adheres to it, by being placed in bags, made of a peculiar kind of woollen fabric, and arranged in frame-work to which a to-and-fro motion is given by machinery, the fine dust passing between the threads of the fabric into a box. The loss thus occasioned amounts on an average to 0·143 per cent., the dust consisting chiefly of charcoal.

Properties of Gunpowder.—Good powder is recognised by the following properties: 1. Its colour should be slate-black; when blue-black it indicates that the powder contains too much charcoal, while a deep black colour shows the powder to be damp. If the charcoal employed was the so-called *charbon roux*, the colour of the powder will be a brown-black. 2. It should not be too much polished so as to shine like burnished black-lead. Small shining specks indicate that the saltpetre has crystallised on the surface. 3. The grains should be uniform in size, unless, of course, two differently sized powders have been mixed. 4. The grain should crack uniformly when strongly pressed, it should withstand pressure between the fingers, and should not be readily crushed to powder when pressed between the hands. 5. When pulverised the mass should feel soft; hard sharp specks show that the sulphur has not been well pulverised. 6. Powder should not blacken the back of the hands or a sheet of white paper when gently rubbed. If it does so, there is either powder-dust or too much moisture. 7. When a small heap of powder is ignited on paper the combustion should be rapid, completely consuming the powder and not setting fire to the paper. If black specks remain, the powder either contains too much charcoal, or it is an indication that that substance has been badly incorporated with the rest of the materials. Yellow streaks left after the ignition show the same defects for the sulphur. If no grains of powder remain, it is a proof that the powder was not well mixed; when any remaining grains of powder cannot be separately ignited, the saltpetre used was impure. If the powder on being ignited sets fire to the paper, it is a proof that it is either damp or of very inferior quality.

Gunpowder can absorb more than 14 per cent. of moisture from the air; if the quantity of water thus taken up is not above 5 per cent., the powder, on being gently dried, reassumes its former activity; but if the quantity of water absorbed exceeds that amount, the gunpowder will not burn off rapidly, and when dried the single grains become covered with an efflorescence of saltpetre, of course impairing the composition and active qualities of the powder. Even what is termed dry powder contains at least 2 per cent. of hygroscopic moisture. Powder can be exploded by a heavy blow as well as by an increase of temperature, and as regards its explosion by a blow, very much depends upon the material upon which it is placed and with which the blow is imparted. The following list exhibits in decreasing order the materials between which a blow most readily ignites powder: Iron and iron, iron and brass, brass and brass, lead and lead, lead and wood, copper and copper, copper and bronze. For this reason gunpowder magazines are provided with doors turning upon bronze and copper hinges, the locks also being of copper. When dry powder is rapidly heated to above

300° it explodes. Even if only a very small portion of the powder is thus rapidly elevated in temperature, the entire quantity, be it large or small, is exploded; hence a very small quantity touched by a red-hot or burning body is sufficient to effect an explosion. It is generally held that the charcoal is first ignited, and that it spreads the ignition to the other materials. Although Mr. Hearder found by experiment that powder does not ignite when touched with a red-hot platinum wire while under the receiver of an air-pump, Professors v. Schrötter and Abel proved that gunpowder so placed ignited rapidly when heated by a spirit-lamp.

Composition of Gunpowder.—Gunpowder consists very nearly of 2 molecules of saltpetre, 1 molecule of sulphur, and 3 of charcoal. Accordingly 100 parts of powder contain—

Saltpetre	74·84
Sulphur	11·84
Charcoal (No. I.)	13·32

The above figures approximately express the composition of the best kinds of sporting and rifle-powder. Ordinary powders, such as blasting-powder, consists of nearly equal molecules of potassium nitrate and sulphur, with 6 molecules of charcoal. Accordingly 100 parts contain—

Saltpetre	66·03
Sulphur	10·45
Charcoal (No. II.)	23·52

Products of the Combustion of Powder.—Drs. Bunsen and Schischkoff found the composition of a sporting and rifle-powder to be, in 100 parts, as follows:

Saltpetre		78·99
Sulphur		9·84
Charcoal, consisting of	Carbon	7·69
	Hydrogen	0·41
	Oxygen	3·07
	Ash	traces

The residue of this powder after combustion was found to consist of—

Potassium sulphate	56·62
„ carbonate	27·02
„ hyposulphite	7·57
„ sulphuret	1·06
Hydrated potassium oxide (caustic potassa)	1·26
Potassium sulphocyanide	0·86
Saltpetre	5·19
Carbon	0·97
Ammonium carbonate, Sulphur	traces
	100·55

It appears from this analysis that the residue left after ignition of the gunpowder consists essentially of potassium sulphate and carbonate, and not, as has been formerly stated, of potassium sulphide. The composition of the smoke of the powder was ascertained to be—

Potassium sulphate	64·29
„ carbonate	23·48
„ hyposulphite	4·90
„ sulphide	—
Caustic potassa	1·33
Potassium sulphocyanide	0·55
Saltpetre	3·48
Carbon (charcoal)	1·86
Ammonium sesquicarbonate	0·11
Sulphur	—
	100·00

From these figures it is clear that the smoke of gunpowder consists essentially of the same substances as the residue from the combustion, the only difference being that the sulphur and potassium nitrate of the powder have been more completely converted into potassium sulphate, while, instead of the potassium sulphide, ammonium carbonate makes its appearance. 100 parts by volume of the gaseous products of the combustion were found to consist of—

Carbonic acid	52·67
Nitrogen	41·12
Carbon monoxide	3·88
Hydrogen	1·21
Sulphuretted hydrogen	0·60
Oxygen	0·52
Nitrous oxide	—
	100·00

The solid residues of combustion formed during the generation of the gases were found to be—

Potassium sulphate	62·10
,, carbonate	18·58
,, hyposulphite	4·80
,, sulphide	3·13
,, sulphocyanide	0·45
,, nitrate	5·47
Charcoal	1·07
Sulphur	0·20
Ammonium sesquicarbonate	4·20
	100·00

The decomposition of powder by its ignition may be represented by the following formulæ:—

1 gramme of powder { Saltpetre 0·789; Sulphur 0·098; Charcoal { C 0·076, H 0·004, O 0·030 } } yields after combustion:

		Grm.
Residue 0·680	K_2SO_4	0·422
	K_2CO_3	0·126
	$K_2S_2O_3$	0·032
	K_2S	0·021
	KCNS	0·003
	KNO_3	0·037
	C	0·007
	S	0·001
	$(NH_4)_2CO_3 + 2(NH_4HCO_3)$	0·028

Gases 0·314		Grm.	c.c.
	N	0·0990 =	79·40
	CO_2	0·2010 =	101·71
	CO	0·0090 =	7·49
	H	0·0002 =	2·34
	SH_2	0·0018 =	1·16
	O	0·0014 =	1·00
0·994			193·10

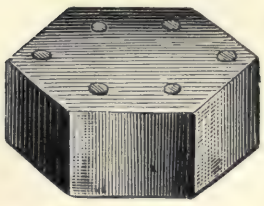
The proportions of the mixtures used in different countries for military powder are:

	Germany.	Russia.	Britain.	France.
Saltpetre	74	75	75	74
Sulphur	10	10	10	10½
Charcoal	16	15	15	15½

Since the American civil war compressed gunpowder has been introduced, especially the so-called "*prismatic powder*." It is merely ordinary powder, which has been compressed in hexagonal moulds. The pressed grain has the shape of a smooth hexagonal prism (Fig. 341) perforated by six tubes. When ignited, the grain burns both from without and from within, in consequence of the tubes. Yet it burns more slowly than finely granulated powder, and imparts a greater force to the projectile.

Testing Gunpowder.—In order to determine the strength or projectile force of gunpowder, and to ascertain which sample is dependent for equality of composition on the mechanical treatment the powder has undergone, the following apparatus are used:—Test mortar, rod testing machine, lever testing machine, ballistic pendulum, and chronoscope. The first of these contrivances is a piece of heavy ordnance, charged with 92 grammes of powder, and a ball weighing 29·4 kilos., the mortar being placed at an angle of 45°. The bore of the mortar is 191 millimetres in diameter by 239 in depth. Powder of good quality should propel the ball a distance of 225 metres, and frequently the ball is carried a distance of 250 to 260 metres. The rod gunpowder testing apparatus consists of a mortar placed vertically, and which, when charged with 22 to 25 grammes of powder, lifts a weight of 8 lbs., made to move between toothed rods; by the height this weight is raised, springs attached to the weight fastening in the notches of the rods and holding it, the quality of the powder is judged.

Fig. 341.



Pyrotechnics.—*Chemical Principles of Pyrotechny.*—Under the name of fireworks we include certain mixtures of combustible substances employed as signals, as destructive agents (for instance, congreve rockets), and for purposes of display.

The various forms are, according to the end in view, so contrived as to burn off either rapidly or slowly, and with more or less emission of gaseous matter, heat, and light. These mixtures are mainly distinguished as heat-producing, ignition communicators (technically termed a fuse), and light-producing. The principle of the rational manufacture of fireworks, applying the word in its extended sense, is that neither any excess of the combustible nor of the combustion promoting and supporting agents should be employed, and that unavoidable accessory materials, viz., such as are intended only to keep the essential ingredients in a certain required shape, the paper casings, &c., be in precisely the quantity required. The best proportions of the combustible and combustion-supporting substances can be readily ascertained by theoretical calculations; for instance, it will be evident that a mixture of 2 equivalents of saltpetre and 1 equivalent of sulphur (1), or a mixture of 2 equivalents of saltpetre and 3 equivalents of sulphur (2), is in each instance wrong; in the latter, too much of the combustible body is used; and in the former case, too much of the supporter of combustion is employed—

(1) S can take up from $2KNO_3$ at most 3O; consequently, 3O remain inactive.

(2) 3S and $2KNO_3$ yield either K_2S and $2SO_3$, or a mixture of K_2SO_4, K_2S, and SO_2, in each case some sulphur remaining unburnt.

We have to bear in mind, however, that it is not always possible to elucidate theoretically the decomposition of firework mixtures, as the affinity of the substances which react upon each other is not well known, and depends on accessory conditions and comparatively unknown influences. It will require a more advanced knowledge of the products of the decomposition of the different substances and their specific heat before we can predict with some degree of certainty the best mixtures. As regards the existing mixtures, they are the result of a lengthy series of experiments, really made by rule of thumb, though with a certain correspondence with the best composition theory can give, that is to say, many of these mixtures have been somewhat modified and improved by modern science.

The More Commonly Used Firework Mixtures.—These mixtures consist mainly of saltpetre, sulphur, and charcoal, either in the same proportions as those in use for gunpowder, or with an excess of sulphur and charcoal. Some mixtures contain, instead of saltpetre, potassium chlorate and other salts, not always essential to the combustion, but

intended either to intensify the light evolved or impart to it a distinctive colour, as in signals and Bengal lights.

Gunpowder is used in fireworks when it is desired that there should be projectile force. A slower combustion of the powder is obtained partly by the use of so-called meal powder, that is, pulverised, not granulated powder, partly by compressing the mixture. If, however, it is intended to produce loud reports, granulated powder is used.

Saltpetre and Sulphur Mixture.—This consists of 2 molecules (75 parts by weight) of saltpetre, and 1 molecule (25 parts by weight) of sulphur, and is used as the chief constituent of such firework mixtures as are intended to burn off slowly and evolve a strong light. However, this mixture is not used by itself, for two reasons, viz., it does not develop a sufficient degree of heat to support its continued combustion, and it does not possess a sufficient projectile force, being capable of producing in the best possible condition of complete ignition only 1 molecule of sulphurous acid—

$$2KNO_3 + S = K_2SO_4 + SO_2 + N;$$

that is to say, 1 part by bulk of this mixture only yields 7·28 volumes of gas. For these reasons the saltpetre-sulphur mixture is employed with charcoal or floury gunpowder.

Grey-coloured Mixture.—Such a mixture, sanctioned by long use, is that known as grey-coloured mixture, consisting of 93·46 per cent. of saltpetre-sulphur and 6·54 of floury gunpowder. This mixture is the chief constituent of other compounds intended to burn slowly, emitting at the same time a brilliant light, owing to the fact that the potassium sulphate formed by the combustion acts similarly to a solid brought to an incandescent state. All mixtures intended to emit light, including coloured lights, are prepared upon the same principle, that the salt which is to give colour shall be non-volatile at the temperature of combustion.

Potassium Chlorate Mixtures; Friction Mixtures; Percussion Powders.—This salt, $KClO_3$, when in presence of combustible substances, gives off its oxygen to the latter more readily, rapidly, and completely than saltpetre; accordingly, this salt is used in all mixtures in which it is desired to combine rapid ignition with combustion. Formerly a mixture of 80 parts by weight of potassium chlorate and 20 parts of sulphur was added to intensify and quicken the combustion of mixtures consisting of more slowly burning salts. A mixture of sulphur, charcoal, and potassium chlorate constitutes an active percussion powder. A mixture of equal parts by weight of black antimony sulphide and potassium chlorate is used for the purpose of discharging ordnance by means of a percussion tube put in the touch-hole of the gun. Sir William Armstrong uses for this purpose a mixture of amorphous phosphorus and potassium chlorate.

Mixture for Igniting the Cartridges of Needle-guns.—This mixture consists either of potassium chlorate and black antimony sulphide, or a compound containing mercury fulminate. The following is a good preparation:—16 parts of potassium chlorate, 8 of black antimony sulphide, 4 of flour of sulphur, and 1 of charcoal powder are moistened with either gum or sugar-water, and about 5 drops of nitric acid added. A small quantity, technically known as the *pill*, is placed in the cartridge and ignited by the friction produced by the sudden passage of the steel needle through it. In this country either the above or a mixture of amorphous phosphorus and potassium chlorate is used. Leaving the silver and mercury fulminates out of the question, the explosive bodies and their applicability to warlike purposes and military pyrotechny have not been sufficiently investigated. Nitromannite or fulminating mannite, the alkaline picrates, and nitroglycerine, of which we shall presently treat more fully, especially deserve notice. M. Dessignolles, who suggests that, instead of saltpetre, potassium picrate should be used in the manufacture of gunpowder, states that quite

different products are formed by the ignition of potassium picrate, when effected in the open air (*a*, or under pressure (*b*):—

a. $\underbrace{2C_6H_2K(NO_2)_3O}_{\text{Potassium picrate.}} = K_2CO_3 + 5C + 3N + NO + NO_2 + 4\,CO_2 + CHN.$

b. $\underbrace{2C_6H_2K(NO_2)_3O}_{\text{Potassium picrate.}} = K_2CO_3 + 6C + 3N + 5CO_2 + 2H_2 + O.$

Fulminating aniline, diazobenzol chromate, obtained by the action of nitrous acid upon aniline, and the precipitation of the product by the aid of a hydrochloric acid solution of potassium bichromate, is, according to MM. Caro and Griess, an efficient substitute for fulminating mercury.

Heat-producing Mixtures.—These consist chiefly of floury gunpowder and grey mixture, to which are added certain organic substances, as pitch, resin, tar, igniting readily, but consumed more slowly than any firework. The heat generated by the combustion of fireworks is much higher than is required to ignite wood, but not of sufficient duration to cause the thorough burning of the wood; hence the addition of tar, &c.

Coloured Fires.—The salts employed to produce coloured flames are—barium, strontium, and sodium nitrates, and the ammoniacal copper sulphate. The so-called cold fuse mixture, composed of grey mixture, flour gunpowder, and antimony sulphide, moistened with brandy and then mixed, produces a white flame. The mixtures for coloured fires used in artillery laboratories are the undermentioned, calculated for 100 parts of each mixture:—

	a. Green.	*b.* Red.	*c.* Yellow.	*d.* Blue.	*e.* White.
1. Potassium chlorate	32·7	29·7	—	54·5	—
2. Sulphur	9·8	17·2	23·6	—	20
3. Charcoal	5·2	1·7	3·8	18·1	—
4. Barium nitrate	52·3	—	—	—	—
5. Strontium „	—	45·7	—	—	—
6. Sodium „	—	—	9·8	—	—
7. Ammoniacal copper sulphate	—	—	—	27·4	—
8. Saltpetre	—	—	62·8	—	60
9. Black antimony sulphide	—	5·7	—	—	5
10. Flour gunpowder	—	—	—	—	15

It is hardly necessary to mention that great care is required in mixing these materials, and that each ingredient ought be pulverised separately.

According to M. Uhden, a beautiful white flame edged with blue is obtained by the ignition of the following mixture:—20 parts of saltpetre, 5 of sulphur, 4 of sulphuret of cadmium, and 1 of charcoal. Thallium chloride with other ingredients yields a beautiful green flame. Magnesium was used during the Abyssinian war in various ways when a brilliant light was required. The chlorates of the alkaline earths and sodium chlorate would be preferable, were it not for the expense, and for the facts that these salts are rather hygroscopic and liable to spontaneous combustion. The barium and strontium carbonates are sometimes used instead of the nitrate. According to MM. Dessignolles and Castelhaz, most brilliant coloured flames are obtained with ammonium picrate in the following proportions:—

Yellow	Ammonium picrate	50
	Ferrous „	50
Green	Ammonium „	48
	Barium nitrate	52
Red	Ammonium picrate	54
	Strontium nitrate	46

More Recent Explosives.—Dessignolles proposes to substitute potassium picrate for

saltpetre in the manufacture of gunpowder. The fearful power of picrate powder, which is also known as Bobœuf powder, Dessignolles powder, and Fontaine powder, is fully known. Mellinite consists essentially of picric acid. Nitromannite,

$$C_6H_8N_6O_{18} = C_6H_8(O.NO_2)_6,$$

is formed on dissolving mannite in fuming nitric acid, and separates out on the addition of concentrated sulphuric acid. It crystallises from boiling alcohol in fine silky needles, which, if heated to 120°, burn with detonation, and explode violently if struck. Nitromannite has been substituted for fulminating mercury as a material for percussion caps. It is said to undergo decomposition on long keeping. Nitrised cane-sugar has been in transient use as an explosive agent under the name Vixorite. Fulminating aniline (diazobenzol chromate), made by the action of nitrous acid upon aniline and precipitating the product with potassium dichromate, has also been proposed as a substitute for mercury fulminate. Hellhoffite is a solution of nitrobenzol in nitric acid.*

Nitroglycerine (nitroleum, pyroglycerine, glyceryl trinitrate, or glonoïne).—This substance was discovered in 1847 by Dr. A. Sobrero, while a student in the laboratory of Professor Pelouze, at Paris. Since the year 1862, M. Alfred Nobel, a Swede, has manufactured this liquid on the large scale. The formula of nitroglycerine is $C_3H_5N_3O_9$ or $\left.\begin{matrix}C_3H_5\\(NO_2)_3\end{matrix}\right\}O_3$; consequently, it consists of glycerine, $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$, in which 3 atoms of H have been replaced by 3 atoms of NO_2. 100 parts of nitroglycerine yield on combustion—

Water	20·0 parts
Carbonic acid	58·0 „
Oxygen	3·5 „
Nitrogen	18·5 „
	100·0 „

As the specific gravity of nitroglycerine is 1·6, 1 part by bulk will yield on combustion—

Aqueous vapour	554 volumes
Carbonic acid	469 „
Oxygen	39 „
Nitrogen	236 „
	1298 „

According to experiments made in Belgium, the combustion of nitroglycerine does not yield free oxygen, but a large quantity of nitrous oxide; hence, the following equation will give some idea of the mode of explosion :—

$$\left.\begin{matrix}\text{2 molecules of}\\\text{Nitroglycerine, } C_3H_5N_3O_9\end{matrix}\right\} = \begin{cases}\text{Carbonic acid, } 6CO_2.\\\text{Water, } 5H_2O.\\\text{Nitrous oxide, } N_2O.\\\text{Nitrogen, } N_4.\end{cases}$$

M. Nobel states that the heat set free by explosion causes the gases to expand to eight times their bulk; accordingly, 1 volume of nitroglycerine will yield 10,384 volumes of gas, while one part by bulk of powder only yields 800 volumes of gas; the explosive force of nitroglycerine is, therefore, to that of powder—

By volume as 13 : 1,
By weight as 8 : 1.

In order to prepare nitroglycerine, very strong nitric acid, density 95° to 98° **Tw.** = 1·476 to 1·49 sp. gr., is mixed with twice its weight of concentrated sulphuric acid, 3300 grammes of this mixture, thoroughly cooled, are poured either into a glass

* Compare Eissler, *Handbook of Modern Explosives*. London : Lockwood & Son.

flask or into a glazed earthenware jar, placed in a pan of cold water, and there is next gradually added 500 grammes of concentrated and purified glycerine, having a density at least of 49° to 51° Tw. = sp. gr. 1·246 to 1·256, care being taken to stir constantly. According to Dr. E. Kopp's recipe (1868) the acid mixture should consist of 3 parts of sulphuric acid at 153° Tw. = 1·767 sp. gr., and 1 part of fuming nitric acid. To 350 grammes of glycerine 2800 grammes of the acid mixture are added; and in performing this operation care should be taken to avoid any perceptible heating for fear of converting by a violent reaction the glycerine into oxalic acid. The mixture is now left to stand for five or ten minutes, and afterwards poured into five or six times its bulk of very cold water, to which a rotatory motion has been imparted. The newly formed nitroglycerine sinks to the bottom of the vessel as a heavy oily liquid, which is washed by decantation; but if not intended for transport—and experience has proved the transport of nitroglycerine to be highly dangerous—the washing may be dispensed with, as neither any adhering acid nor water impairs the explosive properties. Nitroglycerine is now generally made on the spot in America and elsewhere by those whom experience in mining, quarrying, and engineering matters has taught the real value of this very powerful agent.

Nitroglycerine is an oily fluid of a yellow or brown colour, heavier than and insoluble in water, soluble in alcohol, ether, and other fluids; when exposed to continuous cold, not of great intensity, it becomes solidified, forming long needle-shaped crystals. The best means of exploding nitroglycerine is a well-directed blow, neither a spark nor a lighted body will cause the ignition, which even with a thin layer takes place with difficulty, only part being consumed. A glass bottle filled with nitroglycerine may be smashed to pieces without causing the contents to explode. Nitroglycerine may even be gently heated and volatilised without decomposition or combustion, provided violent boiling is carefully prevented. When a drop of nitroglycerine is caused to fall on a moderately hot piece of cast-iron the liquid is quietly volatilised; if the iron is red-hot the liquid burns off instantaneously, just as a grain of powder would do under the same conditions; if, however, the iron is at that heat which will cause the immediate boiling of the nitroglycerine, it explodes with great force. Nitroglycerine, especially if sour and impure, is liable to spontaneous decomposition, which, accompanied by the formation of gas and of oxalic acid, may have been the proximate cause of some of the dreadful explosions of this substance, it being surmised that the pressure exerted by the generated gases upon the fluid in hermetically closed vessels had something to do with the occurrences. On this account M. K. List advises that vessels containing nitroglycerine should be only loosely stoppered, or if being transported provided with safety-valves. Nobel secures nitroglycerine from explosion by dissolving it in pure wood-spirit, from which it may be again separated by the addition of a large quantity of water. Mr. Seeley on this score observes that:—1. The wood-spirit is expensive, and lost in the large quantity of water required for precipitating the nitroglycerine; 2. Wood-spirit, being volatile, may evaporate, and leave the nitroglycerine unprotected; 3. There is a chance of chemical action between these bodies; 4. The vapour of wood-spirit is very volatile, and forms with air an explosive mixture. Many suggestions have been made as to rendering nitroglycerine safe to warehouse; among them may be noted the mixing with pulverised glass in a manner similar to Gale's process for gunpowder. Wurtz recommends the mixture of nitroglycerine with equally dense solutions of either zinc, calcium, or magnesium nitrates, so as to form an emulsion, the nitroglycerine being recovered simply by the addition of water. The taste of nitroglycerine is sweet, but at the same time burning and aromatic; it is a violent poison even in small doses, and its vapour is of course equally virulent, hence great care is required in working with this substance in localities where, as in mines and pits, the supply of fresh air is limited. Instead of manufacturing

nitroglycerine in works specially arranged for that purpose, and transporting this dangerous compound, it is better, as advised by and executed under the direction of Dr. E. Kopp, at the Saverne quarries, to have the quantity required for daily use prepared on the spot by intelligent workmen. Notwithstanding the very serious accidents which have been caused by the explosions of nitroglycerine in this country as well as abroad, and the consequent prohibition of its use, there is no reason why this powerful agent should not be employed according to Kopp's suggestion. Instead of the acid mixture used in the preparation of nitroglycerine, M. Nobel suggests the following:—In $3\frac{1}{2}$ parts of strong sulphuric acid of 1·83 sp. gr. is dissolved 1 part of saltpetre, and the fluid cooled down; the result is the separation of a salt consisting of one molecule of potassa, 4 molecules of sulphuric acid, and 6 molecules of water, and which at 32° F. is altogether eliminated from the fluid, leaving an acid which, by the gradual addition of glycerine, is converted into glonoine, afterwards separated by water, as already described.

Nobel's Dynamite.—Under the name of dynamite, Nobel, in 1867, brought out a new explosive compound, consisting of 75 parts of nitroglycerine absorbed by 25 parts of any porous inert matter, as finely divided charcoal, silica. As evidenced by the experiments of Bolley and Kundt, dynamite has the advantage over nitroglycerine of not being exploded even by the most violent percussion, therefore requiring a peculiarly arranged cartridge. The explosion is attended with such force that large blocks of ice are shattered to atoms. Dynamite burns off quietly in open air, or even when loosely packed, the combustion being accompanied by an evolution of some nitrous acid; but when dynamite is exploded there are generated only carbonic acid, nitrogen, and aqueous vapour, no smoke being formed, and only a white ash left. Dynamite is not affected by damp, and undoubtedly offers great advantages as regards its use in mining, quarrying, and similar operations, for although the price exceeds four times that of powder dynamite performs eight times as much work with less danger and less labour in boring blast holes. The dynamite is placed in cartridges of thick paper, and ignited by means of a fusee, which passes through the sand serving the purpose of a wad. Dynamite can be transported without danger of explosion. Dittmar's dualine is a mixture of nitroglycerine with sawdust or wood-pulp as used in paper mills, both previously treated with nitric and sulphuric acids.

The annual production of dynamite in Europe is now 7000 tons.

Lithofracteur, Dualine, Colonia-powder, Fulminatine, Sebastine, Serranine, Atlas powder, Vulcan powder, Neptune powder, and Forcite are all mixtures containing nitroglycerine.

The gelatine dynamites, which are obtained by dissolving 7 to 8 per cent. of collodion cotton in nitroglycerine, form a solid gelatinous mass, blasting gelatine. It combines the shattering power of nitroglycerine with a more or less decided propelling action, and will doubtless before long supersede dynamite.*

Gun-Cotton.—If cotton is treated with a mixture of nitric acid and sulphuric acid there is formed, according to the proportions and the conditions of action, either gun-cotton or collodion-cotton, bodies which differ considerably in their properties.

Gun-cotton (pyroxiline, fulmicoton) was simultaneously discovered by Schönbein and Böttger. The raw material is cotton, generally the waste of spun cotton freed from all impurities, mechanical and chemical. After being thoroughly torn up and loosened by machinery and dried, it is ready for nitrising.

For this purpose there are used 1 part nitric acid at 1·516 sp. gr. and 3 parts

* The employment of nitroglycerine and its mixtures for criminal purposes is a fatal objection to Kopp's suggestion. These substances should be manufactured only in works carefully constructed and guarded, and should be supplied only to responsible persons.

sulphuric acid at 1·842 sp. gr.; the acids are poured into a large cylindrical vessel of cast-iron, in which revolves an iron shaft fitted with arms driven by conical wheels. After the acids are mixed they are let off into cast-iron vessels, which stand lower, and are closed with covers. Each vessel has a conical bottom with a cock for letting off, from which a branch leads to a common cast-iron main leading to the nitrising room. Here there are thick brick walls in which there is a special cavity for each vessel (at Waltham Abbey a long open channel), in which cold water is constantly flowing. In these cavities there are placed quadrangular cast-iron nitrising vessels, which have a grate at their back part. The quantity of acid used is always twenty times greater than is necessary—about 20 kilos. Into each there is put a small quantity of cotton, about ½ kilo.; it is stirred about with an iron fork, and when nitrised it is hard on the grating. As the cotton, in spite of being pressed, has either consumed or absorbed eleven times its weight of acid, about an equal quantity of fresh acid is added to the vessel. After twenty charges the entire acid mixture will thus have been renewed. The cotton requires a very careful treatment, so as not to obtain portions which have entirely or partially escaped the action of the acid. For this purpose the nitrised cotton is placed in small stoneware pots, set in a cistern constantly traversed by cold water. Here it remains for some time to cool.

At Waltham Abbey the nitrised cotton is whizzed. It is then placed in a large tank of water with a dash-wheel, and is whizzed again. It is then transferred to other washing tanks, each time with fresh water gently heated by steam pipes, to which soda and elutriated chalk are sometimes added to remove the last traces of acid. The cotton is next transferred to a hollander, as they are used in paper-mills, where it is converted into a uniform paste amidst continual washing. Every four hours the water is run off and fresh water is run on. After from twenty-four to thirty-six hours or upwards of such washing a sample of the lot (*potcher*) is tested for its explosion point. If satisfactory, it is once more whizzed and stored for use.

Properties of Gun-cotton.—In its outward appearance gun-cotton does not differ from ordinary cotton, neither is any difference perceptible by microscopic investigation. It is insoluble in water, alcohol, and acetic acid, difficultly soluble in pure ether, but readily soluble in ether which contains alcohol, and in acetic ether. Gun-cotton is liable to spontaneous decomposition, which may even induce its spontaneous combustion; this decomposition is attended with the evolution of aqueous vapour and of nitrous acid fumes, the remaining substance containing formic acid. As regards the temperature at which gun-cotton ignites statements differ; it has in some instances been dried at 90° to 100° without any dangerous consequences, while it has been found to ignite at 43°. Instances are on record of serious explosions of gun-cotton having taken place under conditions which leave no doubt that the greatest care is required in handling and warehousing this substance; for instance, a small magazine, filled with gun-cotton, situated in the Bois de Vincennes, Paris, was exploded by the sun's rays; and at Faversham the Le Bouchet drying rooms, which could not possibly be heated above 45° to 50°, exploded with great violence.* Gun-cotton explodes by percussion, leaving no residue after its ignition. Good gun-cotton may be burned off

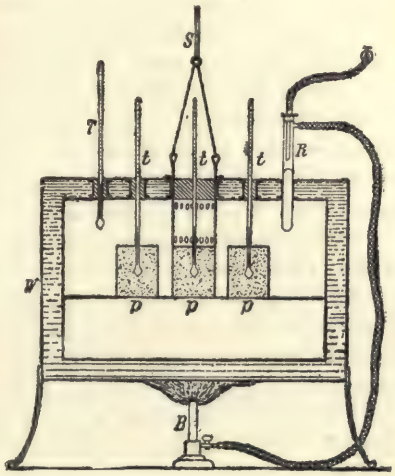
* The extraordinary statements just given are to be explained by the presence of impurities. If the least trace of acid remains the gun-cotton will sooner or later explode spontaneously, even at common temperatures. Or if fatty matter or other impurities are left adhering to the fibre, bye-products are formed which lead to decomposition. The behaviour of gun-cotton when heated depends on the gradual or sudden rise of temperature. In the former case the gun-cotton ignites at a lower point. Cold gun-cotton burns harmlessly if a light is applied to it, but if it has been gradually heated it explodes as if it had been fired by a detonator. The fearful explosion at Stowmarket in 1871 was traced to the malicious addition of acid to some of the finished and dried discs in the magazine.

when placed on dry gunpowder without igniting the latter. It is very hygroscopic, but may be kept for a length of time under water without affecting its explosive properties.

Gun-cotton is generally regarded as trinitro-cellulose, $C_6H_7(NO_2)_3O_5$, but according to Eder it is cellulose hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$; collodion cotton is mainly the tetranitro-cellulose, $C_{12}H_{16}O_6(NO_3)_4$.

The apparatus of Hess for determining the chemical stability of explosives, especially gun-cotton and nitroglycerine, is shown in Fig. 342. The samples, *p*, of the explosives are placed in vessels of badly conductive materials in a heating chest, *W*, with double sides, the intermediate space being filled with water. In the samples is placed a thermometer, *t*, which passes through the chest. The temperature of the heating-room, which can be kept at a suitable point by the burner, *B*, can be read off on the thermometer, *t*; the thermo-regulator, *R*, serves to keep the internal temperature at 70°. The overstepping of the temperature of *t* in the explosives, if found by regular observation, is the consequence of a decomposition, the progress of which is to be regularly followed. Samples of 100 grammes will suffice. In order to make the observation without danger it may be watched from a distance by means of a telescope. The samples, as is shown in the middle vessel, *p*, may be placed in a perforated capsule provided with a cover, and suspended by a flange. It can be raised or lowered into cold water by means of a cord, *S*, passing over pulleys.

Fig. 342.



The examination of gun-cotton is effected by Alberts as follows: the samples are dried for two hours at 40°, then rubbed through a fine sieve of brass wire. An average sample of 10 grammes is then taken and dried in the exsiccator until its weight is constant. The requisite quantity of gun-cotton (about 0·48 gramme), is weighed into a small flask, provided with a glass stopper, and holding about 10 c.c. After the nitrometer (holding 140 c.c.) is prepared as usual, about 5 c.c. pure concentrated sulphuric acid is poured into the flask, the gun-cotton is stirred up in it with a platinum wire, the contents of the flask are emptied as completely as possible into the funnel of the nitrometer, and without loss of time it is drawn into the measuring tube by turning the three-way cock. By repeatedly rinsing out the flask, each time with 3 c.c. of concentrated sulphuric acid, always stirring with the platinum wire, all the rest of the substance is brought into the funnel and thence into the measuring-tube. Lastly, the funnel and the wire are rinsed with sulphuric acid which is also conveyed into the measuring-tube. The three-way cock is closed and the work is complete as usual by shaking.*

* The ordinary way to analyse samples of gun-cotton is to dry a quantity until the weight is constant, and then to weigh 100 grains into a small light flask closed with a stopper, or into a roomy test-tube with a well-fitting cork, an excess of a mixture of 18 parts anhydrous ether and 3 parts anhydrous alcohol is poured upon the gun-cotton, the stopper is inserted and the flask is let stand for 15 minutes, with occasional shaking. The liquid is then poured off and the sample rinsed with a little more of the same mixture. The residue of gun-cotton is allowed to evaporate under the air-pump. If any loss of weight is formed the deficiency is due to a lower compound of cellulose, which has been dissolved out. The remaining quantity is again treated in the same manner with acetic ether, which dissolves the true gun-cotton. If any matter remains undissolved it is cotton fibre which has escaped the action of the acids.

Gun-cotton has been used with success for filtering strong acids, &c., and if steeped in potassium permanganate as an application to wounds which have become offensive.

Collodion Cotton.—Maynard used the solution of gun-cotton in alcohol and ether as an adhesive, and gave it the name of collodion. If it is poured in a thin film upon the skin there is formed on the evaporation of the ether an impervious and adherent layer. It is used in surgery instead of court-plaster for closing up incised wounds, and for the production of photographs on glass (so-called collodion process). Legray produces by the following process a collodion cotton perfectly soluble in ether: 80 grammes of dried and pulverised potassium nitrate are mixed with 120 grammes of concentrated sulphuric acid, and 4 grammes of cotton are thoroughly immersed by the aid of a glass rod or porcelain spatula in the pulpy acid mass, which is stirred about for a few minutes; next the vessel containing acid and cotton is placed in a large quantity of water, and the converted cotton washed until all the acid is eliminated, when it is dried. Soluble cotton may be made with sodium nitrate, 17 parts; sulphuric acid, sp. gr. = 1·80, 33 parts; cotton, ½ part. The converted cotton is soluble in acetic ether, acetate of methyl oxide, wood-spirit, and aceton; the usual solvent is a mixture of 18 parts of ether and 3 parts of alcohol.

Collodion cotton has recently been used in the manufacture of celluloid, a substance which is not explosive, but highly inflammable.

Fulminating Mercury.—The compound known as fulminating mercury is a combination of fulminic acid, an acid unknown in a free state, and of oxide of mercury; its formula may be written $C_2Hg_2N_2O_2$. In 100 parts it consists of 77·06 of peroxide of mercury and 23·94 of fulminic acid. According to the late Dr. Gerhardt's view, this body is a nitro-compound which may be regarded as cyan-methyl, the hydrogen of the methyl of which has been replaced by hyponitric acid and mercury; the formula is then: $C\left\{\begin{matrix}Hg_2\\NO_2\end{matrix}\right\}CN$. This substance was first discovered by Mr. Howard, and was known, until Liebig gave the clue to its nature, as Howard's detonating powder. It is prepared on a large scale in the following manner: First, 2 lbs. of mercury are dissolved, by the aid of a gentle heat, in 10 lbs. nitric acid (sp. gr. 1·33), and 10 lbs. more of nitric acid are then added. The resulting fluid is poured into six tubulated retorts, and to the contents of each retort is added 10 litres of alcohol (sp. gr. 0·833). If the ingredients are mixed by measure instead of weight, for every volume of mercury there is taken 7½ volumes of nitric acid, and 10 volumes of alcohol. After a few minutes a strong evolution of gas takes place, and at the same time a white precipitate, the fulminate of mercury, is formed. The retorts are fitted with tubulated receivers, from which glass tubes carry off the very poisonous gas and fumes, either to a flue or directly to the outside of the shed in which the operation is performed. The precipitate is collected on filters, and washed with cold water to eliminate the free acid. The fulminate is next dried, filtered, and all being placed on plates of copper or earthenware, heated by steam to less than 100°. 100 parts of mercury yield in practice from 118 to 128 parts of fulminate, while, according to theory, 142 should be obtained. The dried fulminate is, with cautious manipulation, divided into small portions, kept separately in a paper bag. The fulminate thus prepared is a crystalline white-coloured substance, which, by being heated to 186°, or by a smart blow, explodes with a loud report. When placed on iron and struck with an iron instrument, the detonation is much increased. This substance also explodes by contact with concentrated sulphuric acid. When mixed with 30 per cent. of its weight of water, the crystalline fulminate may be rubbed to powder with a wooden pestle on a marble slab. The manufacture of this substance on a large scale requires peculiar arrangements, into the particulars of which we cannot here enter.

Percussion-Caps.—The fulminate of mercury is chiefly used for filling percussion-

caps. For this purpose 100 parts of the fulminate are rubbed to powder with 30 parts of water, 50 to 62·5 parts of saltpetre, and 29 of sulphur. This mixture is dried sufficiently to admit of being granulated, after which it is forced, by means of machinery. into the copper caps, and simultaneously covered with either a layer of varnish or tin-foil, to protect it from damp. Tin-foil being more expensive is not used for military gun-caps. The best varnish for the purpose is a solution of mastic in oil of turpentine. The caps are finally dried by a gentle heat, and packed in boxes. One kilogramme of mercury converted into fulminate suffices for the filling of 40,000 gun-caps of the larger or military size, and for 57,600 caps of the size used by sportsmen.

AMMONIA.

The ammonia and the ammoniacal salts employed in the arts are chiefly obtained by the dry distillation of coal. Comparatively small quantities are obtained as bye-products in the manufactures of animal charcoal and of the ferrocyanides; also from stale urine, fæcal waters, from beet-treacle, and from the action of superheated steam upon certain cyanides.

Ammonia, NH_3, consists of 1 volume of nitrogen and 3 volumes of hydrogen, condensing to 2 volumes of ammonia gas, a colourless gas of a peculiar and well-known odour and sharp biting taste. At 15° water absorbs 727, and at 0° 1050, times its own bulk of this gas, the solution being known as liquid ammonia, or spirit of sal-ammoniac, the sp. gr. of which is 0·824 (= 31·3 per cent. NH_3). Usually, however, a weaker and more stable liquid ammonia is prepared for pharmaceutical and technical purposes, having a sp. gr. = 0·960 (= 9·75 per cent. NH_3). The following table shows the specific gravity of liquid ammonia, and the percentage of ammonia contained :—

Specific gravity at 14°.	Per cent. NH_3.	Specific gravity at 14°.	Per cent. NH_3.	Specific gravity at 14°.	Per cent. NH_3.	Specific gravity at 14°.	Per cent. NH_3.	Specific gravity at 14°.	Per cent. NH_3.	Specific gravity at 14°.	Per cent. NH_3.
0·8844	36·0	0·8976	30·0	0·9133	24·0	0·9314	18·0	0·9520	12·0	0·9749	6·0
0·8864	35·0	0 9001	29·0	0·9162	23·0	0·9347	17·0	0·9556	11·0	0·9790	5·0
0·8885	34·0	0·9026	28·0	0·9191	22·0	0·9380	16·0	0·9593	10·0	0·9831	4·0
0·8907	33·0	0·9052	27·0	0·9221	21·0	0·9414	15·0	0·9631	9·0	0·9873	3·0
0·8929	32·0	0·9078	26·0	0·9251	20·0	0·9449	14·0	0·9670	8·0	0·9915	2·0
0·8953	31·0	0·9106	25·0	0·9283	19·0	0·9484	13·0	0·9709	7·0	0·9959	1·0

Ammoniacal gas is abundantly soluble in alcohol. It has numerous technical applications, *e.g.*, in extracting the colouring matters of orchilla-weeds, in the production of ammoniacal cochineal, as an addition in the manufacture of snuff, in purifying coal-gas from carbonic acid and carbon disulphide, in saponifying fats and oils, in the manufacture of ferrocyanides along with carbon disulphide, for dissolving silver (silver chloride) from its ores, in bleach-works, in the manufacture of lakes and colours, and in the production of indigo.

In Java (at the suggestion of Sasser) ammonia has been added to the fermenting mass of indigo and the colour is thus rendered purer.

The uses of ammonia in the ammonia-soda process and in the artificial production of ice are of great importance.

Preparation of Liquid Ammonia.—By decomposing with caustic lime either ammonium chloride or sulphate, ammoniacal gas is set free, and can be absorbed by water, care being taken that the lime is in excess. When ammonium carbonate is prepared on the large scale by the sublimation of a mixture of chalk and sal-ammoniac, a large quantity of ammoniacal gas, 14 parts for each 100 parts of ammonium carbonate, is obtained and may be utilised. Wagner has been the first to observe that the technical preparation of liquid ammonia might be combined with the preparation

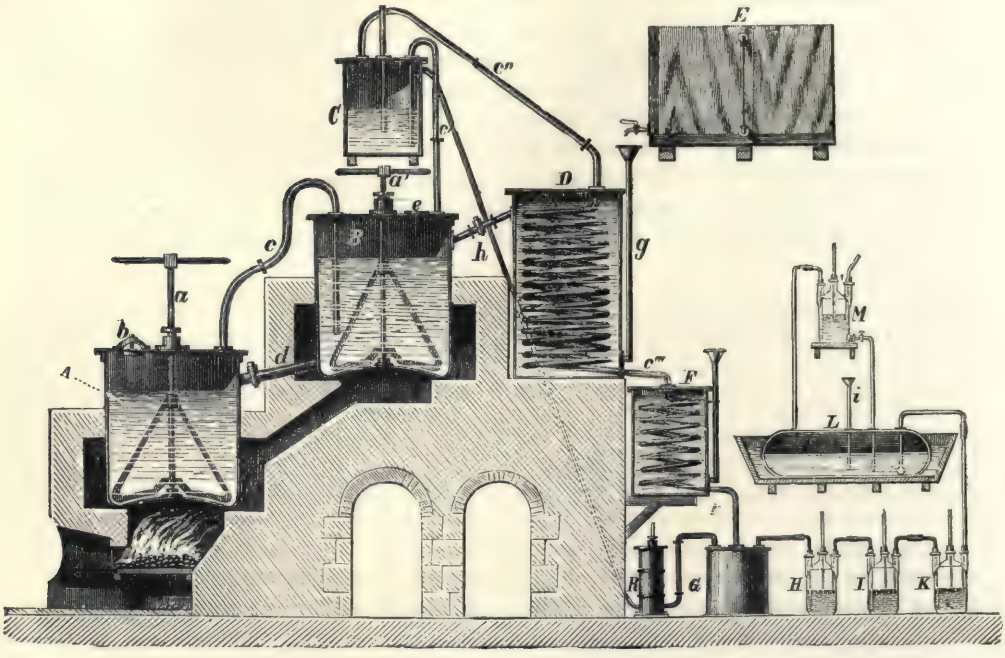
of baryta-white by precipitating a solution of ammonium sulphate with caustic baryta water; the clear supernatant liquor will be a solution of caustic ammonia.

According to Isambert, the reaction taking place during the production of ammonia, $CaO + 2NH_4Cl = CaCl_2 + 2NH_3 + H_2O$, involves a consumption of 10,900 calories. At common temperatures, even in a vacuum, the ammonia escapes from the mixture because there is formed the molecular compound $CaCl_2.2NH_3$, which gives off ammonia only at 180° to 200°. Baryta and strontia drive off ammonia from ammonium chloride at 180° to 200°, whilst it is liberated by litharge at common temperatures.

Inorganic Sources of Ammonia.—1. Native ammonium carbonate, met with in large quantities in the guano deposits of South America, was imported into Germany as a commercial article in 1848. On being analysed this substance was found to consist of —Ammonia, 20·44; carbonic acid, 54·35; water, 21·54; and insoluble matter, 21·54 parts. It is, therefore, an ammonium bicarbonate, $(NH_4)HCO_3$.

2. The preparation in Tuscany of native ammonium sulphate as a bye-product of

Fig. 343.



the preparation of boracic acid has recently become important. The suffioni contain, in addition to boracic acid, potassium, sodium, ammonium, rubidium, &c., sulphates; and that the quantity of these substances is by no means small may be inferred from Travale's researches, from which it appears that four suffioni yielded within twenty-four hours 5000 kilos. of saline matter, consisting of 150 kilos. of boracic acid, 1500 kilos. of ammonium sulphate, 1750 kilos. of magnesium sulphate, 750 kilos. of the ferrous and manganous sulphates, &c. The ammonia is probably due to the decomposition of nitrogenous organic matter, occurring largely in the Tuscan mountains, the soil near the lagoons being impregnated with ammonium sulphate. In combination with the sodium, magnesium, and iron sulphates, ammonium sulphate forms the mineral Boussingaultite, discovered by Bechi.

3. The ammoniacal salts due to volcanic action are of little or no value to industry. Mascagnin, ammonium sulphate, is met with on Vesuvius and Etna; sal-ammoniac is

sometimes also found on Etna, as in the years 1635 and 1669, in such large quantities as to become temporarily an article of commerce at Catania and Messina.

Attempts to convert atmospheric nitrogen into ammonia have led hitherto to no practical results.

Organic Sources of Ammonia.—Industrially speaking, the organic sources of ammonia are far more important than the inorganic. Coal takes here the first place. In the production of coal-gas and of coke, it yields up its nitrogen as ammonia, which is obtained as gas liquor.

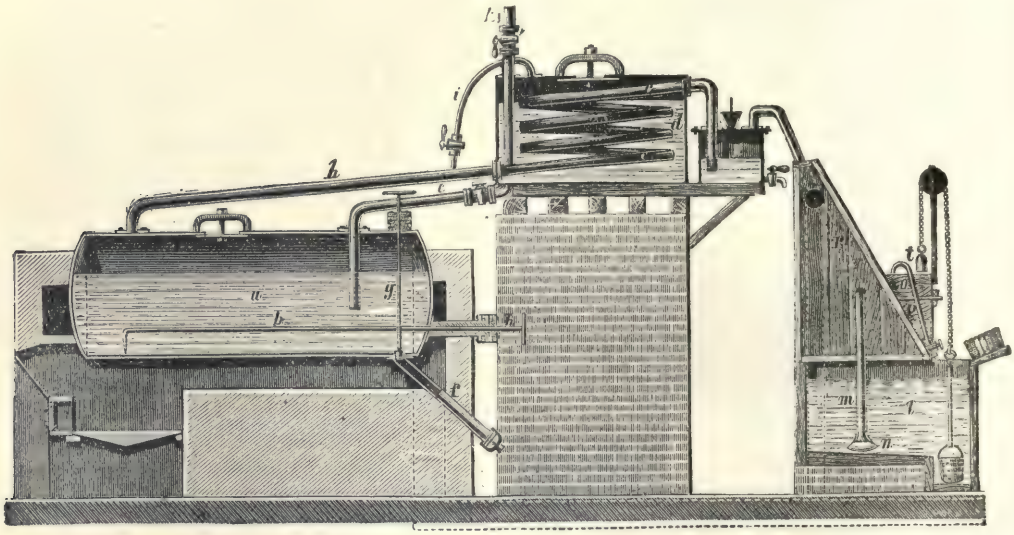
The ammonia of the gas-water may be utilised in various ways. Where fuel is cheap, and crude ammonium sulphate or crude sal-ammoniac a marketable article, the gas-water may be at once neutralised by an acid, and the liquid thus obtained evaporated. This is done in a sal-ammoniac factory at Liverpool, where, during the colder season of the year, 300 cwts. weekly of this salt are prepared. Generally, however, the gas-water is submitted to a process of distillation, and the ammonia evolved converted into sulphate, as in Mallet's apparatus, or into sal-ammoniac, as in Rose's apparatus.

Mallet's Apparatus.—This apparatus, in use in many of the large gas-works, is shown in vertical section in Fig. 343. The plan of action is to force steam into large vessels filled with gas-water, the effect being the volatilisation of the ammonium carbonate. Sometimes lime is added. The volatilised ammonia—of course if lime is added caustic ammonia is evolved—is next conveyed into an acid liquor, and thus converted into ammonium sulphate. The apparatus consists of two cylindrical boiler-plate vessels, *A* and *B*. *A* is heated directly by the fire, and is provided with a leaden tube, *c*, dipping into the liquid contained in *B*, this vessel being placed to catch the waste heat from the fire. *b* and *e* are man-holes; *a* and *a'* stirrers. By means of the tube, *d*, the fluid from *B* can be run off into *A*. Gas-water is poured into both vessels and lime added; ammonia is set free, while calcium carbonate and sulphide are formed, and of course remain in the vessels after the volatilisation of the ammonia. The vessel, *B*, is also filled with ammoniacal water, and when the operation is in progress this water, already warmed, is run by the aid of the tube, *h*, from *D* into *B*. *E* is a gas-water tank, from which *B* is filled by means of *g*. The ammonia set free in *A* is, with the steam, conveyed by the pipe, *c*, into *B*, thence through *c'*, into the wash-vessel, *C*, and thence again through *c''*, into the first condenser, *D*. The partially condensed vapour now passes into the condensing vessel, *F*, the worm of which is surrounded by cold water. The dilute ammonia is collected in *G*, and forced by means of the pump, *R*, into *C*, whence it is occasionally syphoned into either *A* or *B*. The non-condensed ammoniacal gas is carried from *G*, through a series of Woulfe's bottles, the first bottle, *H*, containing olive oil for the purpose of absorbing any hydrocarbons mixed with the gas; the bottle, *J*, contains caustic soda lye, in order to purify the ammonia and retain impurities; the bottle, *K*, is half-filled with distilled water. The ammoniacal gas having passed through *K*, is conveyed to the large lead-lined wooden tank, *L*, filled with dilute sulphuric acid if it is intended to prepare ammonium sulphate, or with water for making liquid ammonia. The vessel, *L*, is placed in a tank of water; *i* is a small pipe for introducing acid; while the tube leading to *M* serves to carry off any unabsorbed ammonia, *M* being also filled with acid.

Lunge's Apparatus.—This apparatus, also intended for the utilisation of gas-water, is shown in Fig. 344; *a* is the boiler; *h* the gas tube connected with the worm, *c*, which is placed in a tank, *d*, filled with gas liquor, run into *a* by means of the tube, *e*. The tube, *f*, is so fitted to *a* as to admit of discharging the waste liquor readily. *b* represents a stirrer fitted to the boiler by a stuffing box, and being intended to rake up the lime and prevent it getting caked to the bottom of *a*; h_1, a tube intended for running gas-liquor into *d*, from a tank placed at a higher level; *i*, a tube provided with a

tap and fitted to the cover of *d*, to convey any gas or vapours from *d* into the worm. *k* represents a wash vessel, sometimes filled simply with water, at others with milk of lime. The gas and vapours having passed through *k*, are conveyed to the absorption vessel, *l*. The tube, *m*, through which the gas passes, is funnel-shaped, and opposite to the mouth of the funnel, at the bottom of the tank, a thick disc of lead is fixed because at this spot the action of the gas would soon wear away the leaden lining

Fig. 344.



of the vessel. *o* is a smaller wooden tank, also lead-lined, into which sulphuric acid is poured, and whence it runs into *l* through the stoneware syphon, *p*. Any vapours given off are caught by the hood, *r*, and thence conveyed by a tube into the chimney. The saline matter deposited in *l* is removed by a leaden pail, as shown in the cut; when this pail is filled it is drawn up by means of the chain and pulley aided by the counter-weight, *t*. The salt (ammonium sulphate) is placed in the basket, *u*, from which the mother-liquor adhering to the salt drains again into the tank, *l*. Evaporation is therefore unnecessary with this apparatus.

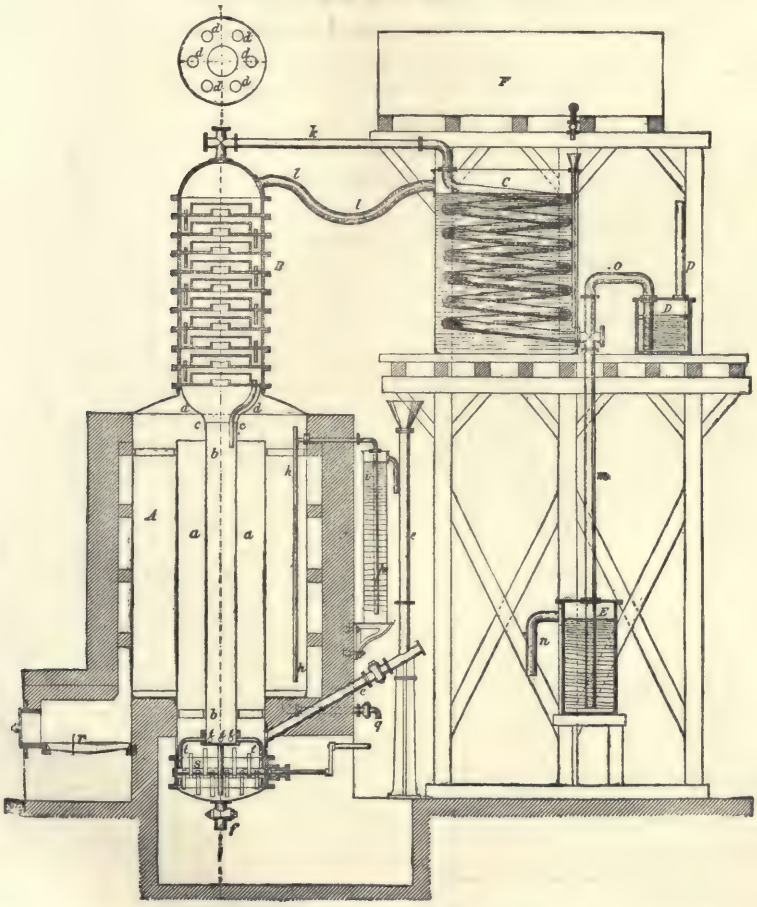
According to Kunheim, the presence of ammonium sulphide is especially troublesome in working up gas liquors. To remove it, and at the same time to utilise all the sulphur, a powerful but greatly subdivided stream of common air is allowed to act upon the cold gas liquor. The ammonium sulphide is then split up into sulphuretted hydrogen and ammonia. The former, along with the excess of air, is passed through finely divided ferrichydroxide and thus absorbed. The hydroxide is suspended in a dilute solution of an alkaline earth.

Among the recent apparatus for distillation the following deserve notice.

The apparatus of H. Grüneberg consists of a still, *A* (Fig. 345 and 346), a rectifier, *B*, a condensing apparatus, *C*, connected with an absorption vessel, *D*, and a hydraulic joint, *E*. The vertical cylindrical pan, *A*, has an internal concentric compartment, *a*, which passes through the lower part of the pan and is prolonged below. It is closed with a vaulted bottom, which latter has an exit cock, *f*, serving to remove the impurities of the lime (introduced through the pipe, *e*, into the cylinder, *a*), as well as to run off the calcium sulphate formed. In the compartment, *a*, the tube, *b*, is suspended concentrically down to the cylindrical affix. This tube, *b*, is closed below and fitted with small outflow tubes, *t*, but above it is connected with the main pan, *A*, by means of the collar, *c*, with its series of perforations at *d*. In the above-mentioned cylindrical

appendage there is a small stirring apparatus, *s*, serving to keep the lime introduced through *e* in close contact with the liquid descending from the internal tube, *b*, through the tubes, *t*, and freed from volatile ammoniacal compounds. The pan, *h*, has an exit pipe, *h*, hydraulically cut off from the cylindrical vessel, *i*, outside the apparatus. It has also an exit-cock, *g*, for complete emptying. Upon the pan, *A*, there is fixed a rectifier of ordinary construction, or in its place a scrubber filled with coke. It is connected with the refrigerator, *C*, by the tube, *k*. The refrigerator is fed from the cistern, *R*. The pipe, *l*, serves to convey away the water which has been warmed in *C* to the rectifier.

Fig. 345 and 346.



The crude gas-liquor flows from *F* into the cooler, *C*, and hence, by means of the tube, *l*, through the rectifier, *B*, into the descending tube of the still-pan, *A*. At the bottom of the piece, *a*, of this pan it meets, whilst flowing down through the pipes, *t*, with the milk of lime which is there present. It is there decomposed, a reaction which is assisted by the occasional movement of the agitator, *s*. The liquid, which now contains free ammonia, rises up in the cylinder, *a*, and flows over at its upper margin into the main pan, *A*. From this it is carried off by the tube, *h*, at the bottom, after the ammonia has been expelled. The vapours evolved in *A* pass through the apertures, *d*, into the rectifier, and from here either into the cooler, *C*, which at the same time separates the gases and the vapours from each other, or, if it is desired to obtain ammonium sulphate, into a lead vessel full of sulphuric acid. In the former case the

ammoniacal liquor condensed in *C* flows through the tube, *m*, into the vessel, *E* (cut off by a hydraulic joint), and flows from there through *n*; the tube, *o*, conveys the uncondensed vapours into the cistern, *D*, lined with lead and filled with sulphuric acid, and from there the gases not absorbed are conveyed into the furnace by the tube, *p*.

Recently the column, *B* (Fig. 347), has been connected with a regulator, *R*. This is an ascending pipe enclosed in a cooling cylinder. It renders it possible to carry off the vapours entering the cooling worm, *D*, as concentrated (as rich in ammonia), as it may be desired by simply regulating the temperature of the refrigerating cylinder, which receives a constant inflow and outflow of cooling water. The more plentiful this flow and consequently the colder the cylinder, *R*, the richer are the ammoniacal vapours issuing from the tube, *k*. To prevent the injurious cooling of the lime vessel and of the steam pipes leading to it, and to supply it with more heat, this lime vessel, *C*, is connected with the still-pan, *A*, and the steam pipes are carried up within the

Fig. 347.

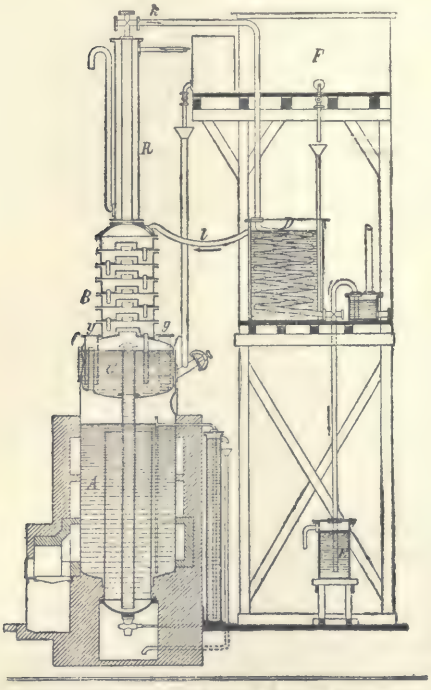


Fig. 348.

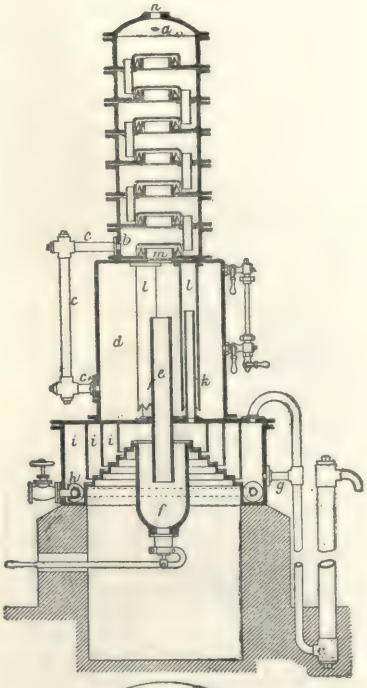
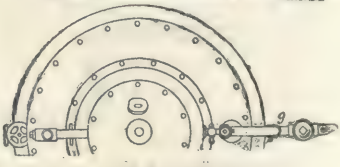


Fig. 349.



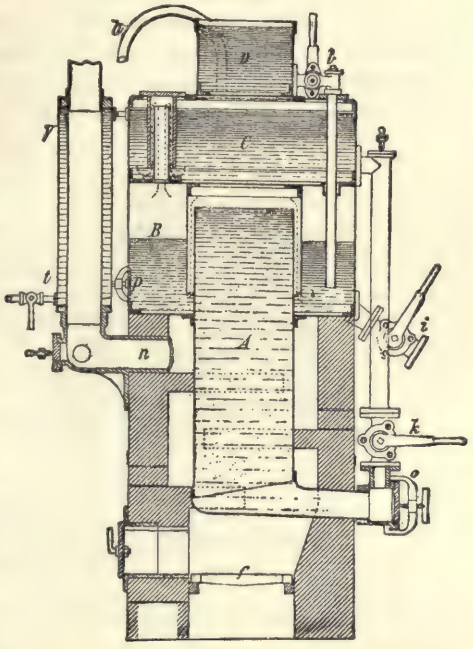
spaces *A* and *C*. This is done in order to keep these parts of the apparatus as hot as possible, and thus accelerate the operation as well as to convey hot vapours into the acid, and thus prevent any further evaporation of the saline lye.

H. Grüneberg and E. Blum further recommend the application of a so-called *stairs column* for gas liquor. The liquid enters above at *a* (Figs. 348 and 349), into the upper column, which it traverses in the opposite direction to the ascending vapours, so that the ammonia is expelled. From the lower column, *b*, the water flows through the pipe, *c*, to the lime-vessel, *d*, where the combined ammonia is set free by the action of milk of lime. The liquid thus treated passes through the pipe, *e*, to the mud bag, *f*, and flows over upon the steps of the column to the outfall, *g*. Inversely the steam serving

in the distillation enters the perforated worm-tube, underneath the stair column, ascends high up the column, being guided by the concentric partitions, *i*; passes through the pipe, *k*, into *l*, which compel the steam to traverse the liquid in the lime pan, and then ascends through *m* to the upper column, which it leaves at *n*, in admixture with the ammoniacal vapours. Thus, the expelled water which contains only a part of the ammonia liberated by the lime, comes, on the stair column, in intimate contact with the fresh steam.

The apparatus of J. Gareis, designed for small gasworks, contains the liquid to be distilled in the two vessels, *A* and *C* (Fig. 350), whilst *B* contains also an addition of milk of lime, admitted from the cistern, *D*. The boiler, *A*, is heated by direct fire in the grate, *b*, and the smoke, &c., escapes through the flue, *n*, into the chimney. The gases and vapours evolving from the liquid in *A*, traverse the liquid mixed with milk of lime in *B*, in the direction of the arrows, heat it to a boil, and pass them in the same manner through the fresh gas liquor in the cistern, *C*, finally arriving through *h* in the condensers, when all the ammonia has been expelled by prolonged boiling from the liquor in *B*; this pan is emptied by opening the cock, *i*, and after closing it again the cock, *k*, is opened, when the liquid in *C* rushes from below into *A*. The liquid here rises up, flows over the upper edge of *A*, and falls into *B*. When this has received the requisite quantity of liquid the cock, *k*, is closed, and by opening the cock, *l*, so much milk of lime is transferred from *D* to *B* as is sufficient for liberating the combined ammonia. The receiver, *C*, is then again filled with fresh gas liquor from a cistern fixed at a higher level. *C* is advantageously filled slowly, say in four hours; to this end the gas liquor, entering at *t*, runs slowly through the warmer, *V*, and arrives in the receiver, *C*. By removing the cover, *o*, the pan, *A*, may be cleaned out as required. For cleaning *B*, there are several small man-holes, *p*. The smallest size of the apparatus works up 1 cubic metre of gas liquor in twenty-four hours, and uses 50 kilos. of waste coke.

Fig. 350.

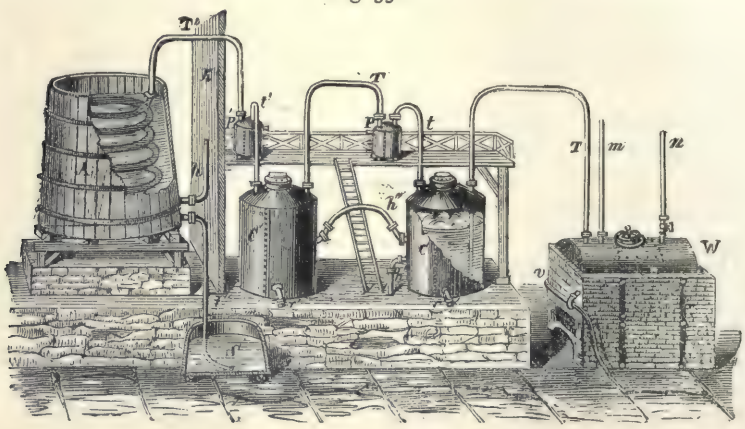


Ammonia from Lant or Stale Urine.—An adult man produces daily on an average 30 grammes urea, representing a yearly yield of 24·2 kilos. ammonium sulphate. Lant, or stale urine, is a very important source of ammonia. Whenever nitrogenous organic bodies are decaying, ammonia is always formed; when the organic substance is a proteine compound, there is formed ammonium carbonate as well as sulphide; but when the organic substance contains no sulphur, only ammonium carbonate is formed, as is the case with the urea, CH_4N_2O, contained in urine, the urea by taking up the elements of the water being converted into ammonium carbonate. Lant is frequently employed without further preparation for various purposes, on account of the ammonium carbonate it contains, as, for instance, in washing wool and removing the fat from flannel and other woollen fabrics.*

* Practical dyers maintain that lant leaves the wool in a better condition for dyeing than pure ammonia or soap, and gives it a more kindly "handle."

The apparatus exhibited in Fig. 351, contrived by Figuera, and until lately in operation at a large establishment for the utilisation of the contents of the latrines and cloacæ of Paris, consists of a steam-boiler, *W*, the steam generated in which is conveyed to two large iron cylinders filled with lant. The ammonium carbonate expelled is, with the steam, condensed in a leaden worm; the cooled liquid is conveyed to a tank filled with acid, and thus converted into ammonium sulphate. The arrangement of the apparatus is as follows :—The wooden vessel, *A*, contains some 250 hectolitres of lant, and is filled by means of the tube, *h*. *C* and *C'* are two cylindrical sheet-iron vessels of 100 hectolitres capacity; *P* and *P'* are similar vessels, the use of which will be presently explained. At the commencement of the operation the boiler, *W*, is filled with about 130 hectolitres of exhausted lant, taken from the vessels *C* and *C'*. The lant in *A*, warm in consequence of having served for condensation, is conveyed to *C* by a tube, and thence by the tube, *h''*, to *C'*, cold lant being poured into *A*. The boiler, *W*, is fitted with three tubes, viz., *T*, the steam pipe, *m*, a safety tube, brought to within a few centimetres from the bottom of the boiler, and carried above the roof of the shed, and *n* a smaller safety tube; *V* is a tube fitted with a stopcock. The steam evolved in *W* is carried by *T* into *C'*, evolving from the liquid therein the am-

Fig. 351.



monium carbonate it holds in solution. The carbonate, with the steam, passes through *t* into the vessel, *P*, which serves to retain any liquid carried over from *C'*. The carbonate of ammonia vapour now passes from *P* through the tube, *T'*, to *C*, and taking up in that vessel more ammonium carbonate, is conveyed through the tube, *T''*, into *P'* (which again serves the purpose of *P*), and thence through *T'''* into the leaden worm of the condensing apparatus. The condensed liquor, a more or less concentrated solution of ammonium carbonate, is run through *t''* into *S*, a wooden vessel, lead lined, and filled with a sufficient quantity of sulphuric acid to saturate the ammonium carbonate. The whole operation lasts about twelve hours; after this time the waste liquid in the boiler is run off by opening the stopcock, *V*, and the operation again repeated. On an average the lant operated upon at Bondy, near Paris, yields per cubic metre from 9 to 12 kilos. of ammonium sulphate, and at each operation 200 kilos. of that salt are obtained by the working of one of the apparatus just described. It is stated that, from the 800,000 cubic metres of urine yearly run waste in Paris alone, there could be obtained, by proper treatment, 700,000 to 800,000 kilos. of ammonium sulphate.

Ammonia from Bones.—By the destructive distillation of animal substances, such as bones, hoofs of horses, refuse horn, skins, hides, decayed meat, &c., there is obtained a series of products, among which ammonium carbonate prevails, with cyanogen compounds, ammonium sulphide, and tarry matter—a very complex liquid containing

pyrrol, bases of the ethylamine series, pyridin, C_5H_5N, picolin, C_6H_7N, lutidin, C_7H_9N, and collidin, $C_8H_{11}N$. The organic matter of these substances contains from 12 to 18 per cent. nitrogen; the organic matter of bones contains 18 per cent. of nitrogen, and, as the organic matter amounts to about one-third of the weight of the bones, these contain about 6 per cent. of nitrogen. Buffalo horn contains 17, waste woollen fabrics 10, and old leather 6·7 per cent. of nitrogen.

It is evident that the quantity of ammonia in the products of the dry distillation of animal substances depends upon the kind and condition of these materials, and upon the temperature at which the operation takes place. The ammonium carbonate is obtained in the condensers as a solid saline mass, the crude hartshorn, or *sal cornu cervi*, or in solution (so called *spiritus cornu cervi*), floating on the surface of the tar. At the present time the manufacture of ammonia and its salts from the products of the dry distillation of animal substances is a matter of but limited industrial importance, owing to the extended coal-gas manufacture. Indeed, dry distillation is now only carried on for the purpose of obtaining animal charcoal, and the occurrence of ammoniacal products is rather considered as a necessary but unavoidable evil. A large quantity of animal matter is used for the manufacture of phosphorus and of prussiates, and in these operations the manufacture of ammoniacal salts is either left altogether out of the question or effected only on a limited scale.

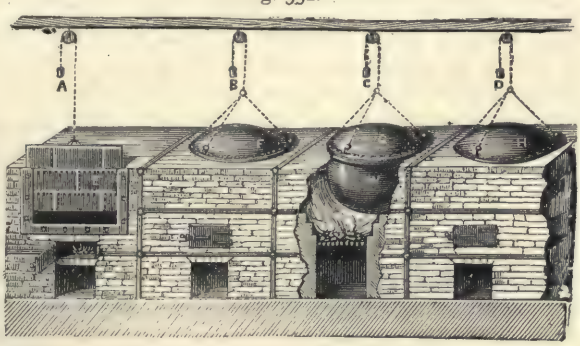
Ammonia from Beet-Sugar.—When the beet-root juice is boiled, ammonia is evolved in large quantities, and may be utilised in the preparation of ammonium sulphate. The ammonia yielded by the juice is the product of the decomposition of the aspartic acid and betain present in the roots. According to Renard, a beet-root sugar manufactory which yearly consumes 200,000 cwts. of beets might thus obtain 887 cwts. of ammonium sulphate.

Technically Important Ammoniacal Salts.—*Sal-ammoniac, ammonium chloride*, NH_4Cl, consists 100 parts of—

Ammonia,	31·83	Ammonium,	33·75
Hydrochloric acid,	68·22	Chlorine,	66·25

From the thirteenth to the middle of the eighteenth century this salt was imported into Europe exclusively from Egypt, where it was obtained by the combustion of camel's dung. The camel feeds almost exclusively upon plants containing salts, and the sal-ammoniac is sometimes found ready formed in the animal's stomach. The sal-ammoniac having sublimed with the soot from the combustion of the dung, was collected and refined by a second sublimation.

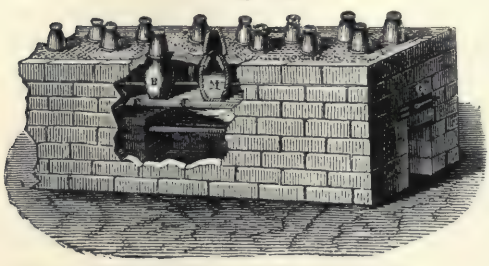
Fig. 352.



In localities where dung is used as fuel, it has been tried to obtain sal-ammoniac by combustion with common salt. The first sal-ammoniac manufactory in Germany was established by Gravenhorst Brothers, at Brunswick, in 1759. We have already seen how crude sal-ammoniac may be prepared from gas-water or by other means. The salt, no matter whence derived, is purified by sublimation in cast-iron cauldrons, W, Fig. 352, lined with fire-clay. As soon as the crude sal-ammoniac is put into these vessels and tightly rammed, heat is applied, at first gently, so as to drive off any

moisture. This effected, iron lids, F, G, H, are luted to the cauldrons; the lids can be readily moved by means of the pulleys and chains provided with counter-weights, B, C, D. Instead of iron covers lead hoods sometimes are employed, the opening of which is temporarily closed with an iron disc. The hoods or covers are always securely fastened to the cauldrons, to prevent them being forced off by the pressure of the vapours. The temperature has to be regulated during the process with great nicety, for too low a degree of heat yields a loose salt, and with too high a degree of heat the organic matter present in the crude sal-ammoniac is liable to give off empyreumatic matter, spoiling the appearance of the sublimed salt and interfering with its good quality. Experience has proved that it is expedient to have the sublimation vessels of rather large size, $2\frac{1}{2}$ to 3 metres interior diameter. When the sublimed sal-ammoniac cake has attained a thickness of 6 to 12 centimetres the operation is discontinued and the cake removed. The furnace is provided with an oven for drying the sal-ammoniac, this oven being shut with a door, E, movable by means of a chain running over a pulley, and aided by a counterpoise. At the present day sal-ammoniac is often sublimed in earthenware vessels or large glass flasks, the crude salt being first mixed with 20 to 30 per cent. of its weight of powdered animal charcoal, then dried over a good fire, and next put into the stoneware sublimation vessels, B and M, Fig. 353, placed in two rows over the fire-place, G. Each of these vessels is 50 centimetres in height; the openings are surrounded by an iron plate properly fitted to the neck and provided with a flange upon which rest the earthenware vessels wherein the sublimed sal-ammoniac is condensed. When glass flasks are used, the height of these vessels is 60 centimetres by 30 centimetres diameter. Sixteen of these flasks, each charged with 9 kilos. of the mixture of sal-ammoniac and charcoal, are placed upon a furnace in cast-iron pots, which are filled with sand. The cover is in this case a leaden plate. The sublimation is carefully conducted, and goes on slowly, lasting about twelve to sixteen hours. After this time, the leaden plates are removed, bungs or plugs of cotton-wool inserted, and the flasks allowed to cool very gradually, for as the salt expands on cooling the glass vessels may be broken. The cake of sal-ammoniac when quite cool is scraped clean with a knife, and afterwards presents a perfectly crystalline appearance. When it is desired to obtain the salt free from iron, the crude salt should be mixed, before sublimation, with about 5 per cent. of superphosphate of lime, or with 3 per cent. of ammonium phosphate; by this addition any iron chloride is decomposed and left in the retort as phosphate. The sal-ammoniac of commerce is met with either in a crystalline state or as a compact fibrous sublimed material; in the latter case the cakes or discs have a meniscus shape, weigh abroad from 5 to 10, but in England usually about 50 kilos., and exhibit the appearance of having been formed in layers. Crystalline sal-ammoniac is obtained by adding to previously re-crystallised sal-ammoniac a boiling hot and saturated solution of the same salt, so as to form a thickish magma, which is next placed in moulds similar in shape to those in use for making loaf-sugar; after draining, the loaf of sal-ammoniac is removed, dried, and packed in paper ready for sale. Besides the use made of sal-ammoniac in chemical laboratories, by pharmaceutists and veterinary surgeons, it is industrially in demand for tinning, zincing, and soldering, in calico-printing and dyeing, in the manufacture of paints and pigments, in the preparation of platinum, snuff, and very largely in the preparation of a mastic—

Fig. 353.



1 part of sal-ammoniac, 2 of sulphur, and 50 of iron filings—used in joining steam-pipes, the sockets and spigots of iron gas- and water-pipes, &c. Sal-ammoniac is also employed in the preparation of pure *ammonia liquida* and ammoniacal salts.

Ammonium Sulphate.—It has been already mentioned that ammonium sulphate, $(NH_4)_2SO_4$, is met with native in small quantities in the mineral known as mascagnin, in larger quantities in the boracic acid of Tuscany, while it is also found in Boussingaultite.

The modes of preparing this salt from the ammoniacal water of gas-works, lant, the products of the dry distillation of bones, by the aid of sulphuric acid, or by double decomposition by means of gypsum or iron sulphate, have been already given. The concentration of the weak solution by evaporation yields the crystalline salt, which, however, when obtained from liquors containing tarry matters is usually of a deep brown colour, and has therefore to be purified by being dissolved in hot water, filtered through animal charcoal, and then re-crystallised, the best plan being to evaporate the solution rapidly, and remove the salt gradually by means of perforated ladles. The salt is then drained by being placed in baskets, and next quickly dried on heated fire-clay slabs, in which operation any particles of tar are decomposed. Sulphite of ammonia obtained by saturating ammonium carbonate solution with sulphurous acid gas is, when exposed to air, gradually converted into sulphate. Ammonium sulphate is, industrially speaking, far the most important of the ammonia salts, because besides being very largely used in artificial manure mixtures, and by itself for the same purpose, it is extensively employed in alum-making, and is the starting-point of the preparation of ammonium chloride, ammonium carbonate, liquid ammonia, and other similar products.

Ammonium Carbonate, as met with in commerce, was formerly supposed to be ammonium sesquicarbonate, but the investigation of H. Vogler, in 1878, showed that it is approximately a mixture of ammonium bicarbonate and carbaminate.

The salt used in pharmacy and industry under this name is in reality ammonium sesquicarbonate, and composed according to the formula

$$(NH_4)_4C_3O_8, \text{ or } 2([NH_4]_2CO_3) + CO_2.$$

It is obtained either directly from the products of the distillation of bones, or by subliming a mixture of chalk and sal-ammoniac.

Among the products of the dry distillation of bones is found a solid sublimate, essentially impure ammonium carbonate, purified by sublimation. For pharmaceutical use ammonium carbonate is prepared by submitting a mixture of either ammonium chloride or sulphate with chalk—4 parts of the ammonia salt, 4 of chalk, and 1 of charcoal powder—to a low red heat. The product is a perfectly pure white salt; during the operation a large quantity of ammoniacal gas is evolved, which is either absorbed by water or by coke moistened with sulphuric acid. Kunheim decomposes the sal-ammoniac by subliming it with barium carbonate, barium chloride being obtained as a bye-product. When freshly prepared, ammonium carbonate is a transparent crystalline mass, which, while absorbing water from the atmosphere, and evolving ammonia, is superficially converted into ammonium bicarbonate (ammonium hydrocarbonate, $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}CO_3$). Owing to the penetrating odour emitted by this salt, it is known as smelling salts. Impure ammonium carbonate is also used for cleaning woollen and other fabrics, for the removal of grease from cloth, and further, for the production of the orchil pigments. Pure ammonium carbonate, besides its use in pharmacy, is an ingredient of baking and yeast powders.

Ammonium Nitrate.—This salt, $(NH_4)NO_3$, is prepared by the double decomposition of solutions of ammonium sulphate and potassium nitrate. The potassium sulphate is first separated, and the solution of ammonium nitrate having been concentrated by

evaporation is left to crystallise, its crystalline form being similar to that of saltpetre. When dissolved in water this salt produces cold, and is therefore used in freezing mixtures; while the fact that when strongly heated it is converted into nitrous oxide and steam ($N_2O + 2H_2O$) might perhaps render it of use in the preparation of a blasting powder.

The manurial value of ammoniacal salts is, according to C. O. Harz, higher than it is commonly assumed. Barley, rice, clover, peas, flourish better with ammoniacal manures than with nitre. The behaviour of maize and oats is the reverse; wheat and barley take an intermediate position, wheat inclining more to ammonia.

PHOSPHORUS.

Phosphorus is widely distributed in nature as phosphates. The most important phosphatic mineral is Apatite, $Ca_5Cl(PO_4)_3$, which as Phosphorite and Staffelite forms massive deposits; less abundant are Vivianite, $Fe_3(PO_4)_2.8H_2O$; Turquoise, $Al_2PO_4(OH)_3H_2O$, and pyromorphite, $Pb_5Cl(PO_4)_3$. Phosphorus is a frequent constituent of iron ores and a very important ingredient of agricultural soils, being necessary for all cultivated plants. Phosphorus is also an indispensable constituent of the animal body—*e.g.*, of the brain; the bones consist chiefly of calcium phosphate.

Preparation of Phosphorus.—Bone-ash is now the only material used by phosphorus makers, as the commercial preparation of phosphorus has not succeeded by using either apatite and other varieties of pure phosphorite which contain about 18·6 per cent. of phosphorus—as well as sombrerite (a mineral met with on the American island of Sombrero), consisting of calcium phosphate and carbonate, and imported into England for the manufacture of superphosphates; or the Navassa guano, also imported from the United States, containing, according to Ulex's researches, one-third of its weight of phosphoric acid; or iron phosphate, as proposed by Minary and Soudray, by distilling that substance with previously well-ignited coke-powder.

Bones, as used by the manufacturers, contain:—

In dry state, but not ignited,	from 11 to 12·0	per cent.	of phosphorus.
As bone-black	„ 16 to 18·0	„	„
As bone-ash (white burnt bones)	„ 20 to 25·5	„	„

The composition of bone-ash is exhibited by the following results of analysis:—

	1.		2.
Calcium carbonate	10·07	...	9·42
Magnesium phosphate	2·98	...	2·15
Tricalcium phosphate	83·07	...	84·39
Calcium fluoride	3·88	...	4·05

The bone-ash is decomposed by means of sulphuric acid, according to a plan first suggested by Nicolas and Pelletier:—

a. Bone-ash, $Ca_3(PO_4)_2$ / Sulphuric acid, $2H_2SO_4$ } yield { Acid calcium phosphate, $CaH_4(PO_4)_2$ / Calcium sulphate, $2CaSO_4$.

The acid calcium phosphate is heated with charcoal, and converted by loss of water into calcium metaphosphate:—

$$b.\ \underbrace{\left.\begin{matrix}Ca\\H_4\end{matrix}\right\}(PO_4)_2}_{\text{Acid calcium phosphate.}} = \underbrace{Ca(PO_3)_2}_{\text{Calcium metaphosphate.}} + 2H_2O.$$

Calcium metaphosphate yields, when ignited to a white heat with charcoal, two-thirds of its weight of phosphorus, while one-third remains in the residue—

c. Calcium metaphosphate, $3Ca(PO_3)_2$ } yield { Tribasic calcium phosphate, $Ca_3(PO_4)_2$
Charcoal, 10C { Carbonic oxide, 10CO
{ Phosphorus, 4P.

The ordinary mode of preparing phosphorus includes the following operations:—

In some instances the preparation of phosphorus is cotemporary with other businesses, viz., glue-boiling, the preparation of sal-ammoniac, yellow prussiate of potash, &c., but generally in England the phosphorus makers do not even burn the bones to ashes, but purchase bone-ash and occasionally apatite; this salt, however, is very difficult to treat with sulphuric acid, and is also objected to on account of its hardness, for it has to be ground to a very fine powder. English makers only carry out these four processes:—

1. Burning the bones and grinding the bone-ash to powder.
2. Decomposition of the bone-ash by sulphuric acid, and evaporation of the acid phosphate previously mixed with charcoal.
3. The distillation of the phosphorus.
4. The refining and preservation of the phosphorus.

Burning of the Bones to Ash.—1. The bones to be used for phosphorus making are obtained either from bone-boilers or from the waste bone-black of sugar-refiners. The aim of the ignition of the bones is the complete destruction of the organic matter. The operation is conducted in a kiln very similar to those in use for burning lime. A layer of brushwood having been put at the bottom of the kiln, bones form the next stratum, and so on alternately. The wood having been lighted, the combustion of the bones ensues. In order to carry off the fumes, the smell of which is very offensive, a hood made of boiler-plate is placed on the kiln, and either connected with a tall chimney, or the smoke and gases are conducted into the fire of the kiln and burnt. The white burnt bones are withdrawn through an opening reserved in the wall on purpose, the kiln being kept continuously in operation, as is the case with some lime-kilns.

100 kilos. of fresh bones yield from 50 to 55 kilos. of white burnt bone-ash, which is converted into a coarse powder by means of machinery.

Decomposition of the Bone-ash by Sulphuric Acid.—2. 100 kilos. of the bone-ash, of which about 80 per cent. is tribasic phosphate, require for decomposition:—

106·73 kilos. sulphuric acid of 1·52 specific gravity.
85·68 „ „ „ 1·70 „
73·63 „ „ „ 1·80 „

Payen advises that for 100 kilos. of bone-ash 100 parts of sulphuric acid at 50 per cent. or 1·52 sp. gr. be taken. The operation of mixing the acid and bone-ash is effected in lead-lined wooden tanks, or in wooden tubs internally coated with pitch or coal-tar asphalte. The liquor decanted from the precipitate has a sp. gr. of 1·05 to 1·07 = 12° to 14° Tw. The sediment is lixiviated with water, and the liquor obtained (= 6° to 8° Tw.) evaporated with the first liquor in leaden pans. A second lixiviation of the sediment yields a fluid which is used instead of water for the purpose of diluting the oil of vitriol. The evaporation in the leaden pans (these are smaller, but otherwise similar in construction to those used for evaporating sulphuric acid) is continued until the fluid has attained a sp. gr. of 1·45 = 84° Tw., when it is mixed with charcoal-powder, or rather granulated charcoal, of the size of small peas, in the proportion of 20 to 25 parts of charcoal to 100 of liquor, and quickly dried after having been put into cast-iron pots placed on a furnace.

The dry mass consists of phosphate of lime, carbon, and water, to an amount of 5 to 6 per cent. At the commencement of the manufacture of phosphorus the idea prevailed that in the preceding preparation the phosphoric acid was present in the free state, while the lime had combined with sulphuric acid; but Fourcroy and Vauquelin finding that the tribasic calcium phosphate as met with in bone-ash ($Ca_3(PO_4)_2$) was, by

the action of the sulphuric acid, converted into acid calcium phosphate ($CaH_4(PO_4)_2$), supposed that more sulphuric acid was required, an opinion opposed by Javal, who proved that when pure phosphoric acid is intimately mixed with carbon, it yields only a small quantity of phosphorus, because the acid is volatilised at a temperature lower than that required for its decomposition, or rather reduction by carbon. Owing to the presence of water in the mixture, there is given off during the distillation in addition to oxide of carbon, hydrogen carbide and phosphide.

Distillation of Phosphorus.—3. The mixture of acid calcium phosphate and charcoal is distilled in fire-clay retorts similar in shape to those used for distilling Nordhausen sulphuric acid, while the furnace in which these retorts are placed is also similar in construction and holds twelve retorts on each side. The body of the retorts is placed on the side of the fire, while the neck passes through an opening in the wall of the furnace, that portion of the wall being only lightly bricked up, as the retorts, after the distillation is finished and the furnace cooled, have to be removed, in order to clear out the residue and introduce fresh mixture. Between each pair of retorts is left a space of some 12 to 15 centimetres, in order to afford room for the passage of the flame. As already mentioned, the heat causes the acid calcium phosphate, ($CaH_4(PO_4)_2$), to be converted into calcium metaphosphate, ($Ca(PO_3)_2$), which, with increased heat, gives off two-thirds of its phosphorus, there being left in the retorts one-third in the shape of calcium triphosphate, ($Ca_3(PO_4)_2$). The receivers used in Germany are constructed in the following manner :—The material is clay, glazed. The receiver consists of two parts, one of which is a cylindrical vessel open at the top, into which the other part fits, and is fixed by means of a rim which is prolonged so as to form a neck, between which and the first part is inserted a tube fitted on the neck of the retort, while the other end of this tube dips for about 10 centimetres into the receiver, the latter being filled with water. Into each retort 6 to 9 kilos. of the mixture intended to be operated upon are introduced ; the retorts are then placed in the furnace and the brickwork is restored. This having been done, the fire is kindled and kept up very gently for some time in order to dry the fire-clay used in joining the bricks. The receivers are filled with water and fitted to the retorts. In each receiver a small iron spoon is placed fastened to an iron wire which serves as a stem. After six to eight hours' firing the heat has been so much increased as to cause the expulsion of any moisture left in the material placed in the retorts, while quantities of hydrocarbon gases and oxide of carbon are formed and expelled with the sulphurous acid. Subsequently other gases are given off, and because they contain some hydrogen phosphide are spontaneously inflammable. As soon as this phenomenon is observed, the joints of the receivers and apparatus connecting it with the retort are luted with clay, care being taken to leave, by the insertion of an iron wire, a small opening for the escape of the gases, which are as speedily as possible removed by well-arranged ventilators from the building in which the furnace is placed. The appearance of amorphous phosphorus at the small opening indicates the commencement of the distillation. The spoon is then placed in the receiver in such a direction that any phosphorus coming over may collect in it. During the progress of the operation, and as long as any phosphorus distils over, the evolution of combustible gases continues, and consequently a small blue-coloured flame is observed at the opening in the lute. The water in the receivers is kept cool during the operation. After forty-six hours, with a greatly increased firing, a full white-heat is reached, and the quantity of phosphorus coming over has decreased so much as to make a continuation of the ignition process wasteful. The receivers are therefore disconnected from the retorts, and the crude phosphorus, a mixture of phosphorus, phosphorus silicide and carbide, amorphous phosphorus, and other allotropic modifications of this element, is poured into a tub containing water. The furnace having become cool is broken up and the retorts are removed, the contents taken out

with an iron spatula, and the retorts replaced after having been re-filled with fresh mixture. 100 kilos. of the mixture yield about 14·5 kilos. of crude and 12·6 kilos. of refined phosphorus. As to Wöhler's method of preparing phosphorus by the ignition of a mixture of charcoal, sand, and bone-ash, the process is not well adapted for practical use, because it requires a very high temperature, which would melt, or nearly so, and at any rate soften, the retorts. Moreover, the proposed mixture contains only one-third the quantity of phosphoric acid met with in the mixture now in general use.

Refining and Purifying the Phosphorus.—4. As already stated, the crude phosphorus is contaminated with carbon, silicon, red and black phosphorus, and various other impurities, which in former days were eliminated by forcing the phosphorus through the pores of stout wash-leather by means of a machine exhibited in Fig. 354, C representing a tightly tied piece of wash-leather containing the crude phosphorus,

Fig. 354.

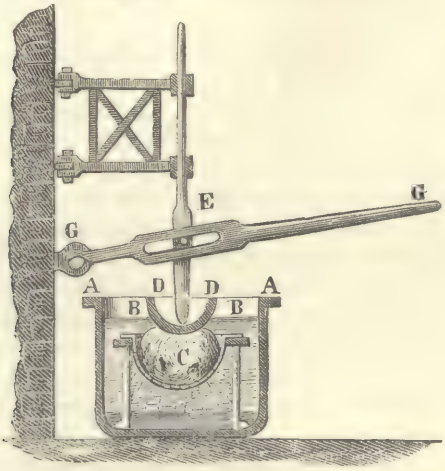


Fig. 355.

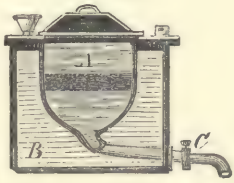
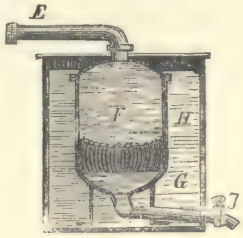


Fig. 356.



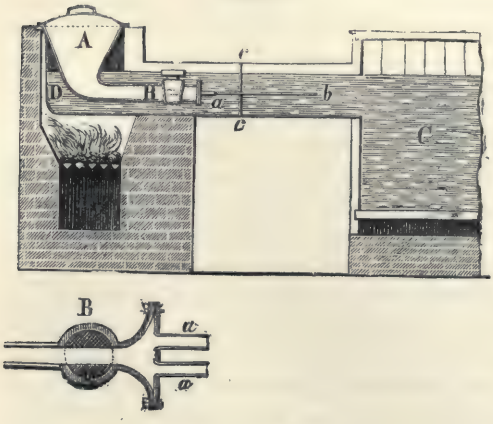
the bag being placed on a perforated copper support, situated in a vessel filled with water at 50° to 60°. As soon as the phosphorus is molten, there is placed on the wash-leather a wooden plate, D D, which by the aid of the mechanical arrangement E, and the lever, G G, can be forced downwards so as to cause the fluid phosphorus to pass through the pores of the leather, the impurities being retained. More recently French manufacturers have introduced another system of purifying phosphorus, viz. :—*a*. By filtration through coarsely powdered charcoal, which is placed in a layer of 6 to 10 centimetres on a perforated plate of the vessel, *A*, Fig. 355, two-thirds filled with water, kept by means of the water-bath, *B*, at a temperature of 60°. The molten phosphorus placed on *A* passes through the layer of charcoal, and is thereby purified. It flows through the open tap, *C*, and the tube, *E* (Fig. 356), being collected in the vessel, *F*, filled with water, maintained by means of the water-bath, *G*, at a temperature sufficiently high to render the phosphorus fluid, so that it may, when aided by hydraulic pressure, pass through the perforated bottom, *H*, and the wash-leather spread over it. The filtered phosphorus may be run off by means of the tap, *J*.

According to another process of purification (*b*), porous, unglazed porcelain or earthenware plates are fixed in an iron cylinder connected with a steam-boiler. The steam yielded by the latter forces the molten phosphorus—previously mixed with charcoal powder for the purpose of preventing the pores of the plates becoming choked—through the earthenware plates. The charcoal containing some phosphorus is used in the distillation of the phosphorus. This method of purification yields from 100 kilos.

of crude, 95 kilos. of refined, phosphorus. In Germany crude phosphorus is purified by distillation, this operation being carried on in iron retorts of a peculiar make, and shaped like the glass retorts used in chemical laboratories. The neck of these retorts dips for a depth of 15 to 20 millimetres in water contained in a basin filled to the rim, so that any phosphorus which is discharged into this water causes it to overflow. The crude phosphorus having been fused under water is next mixed with 12 to 15 per cent. of its weight of moist sand, and this mixture is placed in the retorts in quantities of 5 to 6 kilos., the object of the mixing with sand being to prevent the phosphorus becoming ignited during the filling of the retorts. Crude anhydrous phosphorus yields by this process of distillation about 90 per cent. of the refined product. In a phosphorus manufactory at Paris the crude phosphorus is purified by chemical means—viz., by mixing with 100 kilos. of the crude substance 3·5 kilos. of sulphuric acid and the same quantity of bichromate of potash; a slight effervescence ensues, but the result is that the phosphorus is rendered very pure, and may, after washing with water, be at once cast in the shape of sticks. The yield of refined phosphorus by this process is 96 per cent.

Moulding the Refined Phosphorus.—It has long been the custom to mould phosphorus into the shape of sticks formed by the aid of a glass tube open at both ends, one of these being placed in molten phosphorus covered by a stratum of warm water. The liquid phosphorus is sucked by the operator into the tube until it is quite filled. The lower opening of the tube being kept under water is closed by the finger of the operator; the tube is instantly transferred to a vessel filled with very cold water, by which the phosphorus is solidified. It is removed from the glass tube by pushing it out with a glass rod or iron wire while being held under water. Instead of suction by the mouth, a caoutchouc bag similar to that used in volumetric analysis for the purpose of sucking liquids into pipettes may be employed. In the French phosphorus works the glass tubes are fitted at the top with an iron suction tube provided with a stop-cock. The operator, who has from one to two thousand of these tubes at his disposal, sucks, either by mouth or with a caoutchouc bag, the molten phosphorus into the glass tube, and having turned off the stop-cock, rapidly transfers the tube to a vessel filled with cold water. When all the tubes are filled the phosphorus is removed by opening the stop-cock and pushing the stick out by the aid of a wire. A clever workman may mould in this way 2 cwts. of phosphorus daily.

Fig 357.



Another mode of performing the moulding has been introduced by Seubert. The apparatus contrived by him for this purpose is exhibited in Fig. 357, and consists of a copper boiler fitted on a furnace; to the flat bottom of this boiler is fastened by hard solder an open copper trough communicating with the water-tank, C. In the boiler is fitted a copper funnel, A, provided with a horizontal tube, B. This portion of the apparatus is intended for the reception of the phosphorus, of which it will hold 8 to 10 kilos. At the end of the horizontal tube is placed a stop-cock, B, while the portion of the projecting mouth of the tube beyond the cock is widened out and fitted by means of bolts and nuts, with a flange-like copper plate, into which are inserted two glass tubes, *a a*. Into the copper trough is let a wooden partition,

c c, which serves the purpose as well of supporting the glass tubes as of preventing the communication of the hot water in the boiler and a portion of the trough with the cold water of the tank and the portion of trough nearest to it. The vessel A having been filled with refined phosphorus, the water in D is gently warmed so as to cause the fusion of the phosphorus. As the warm water reaches to the partition, *c c*, it is clear that on opening and closing the tap B, some phosphorus will pass through and flow out of the tubes *a a*, but that remaining in these tubes will solidify, and on opening the tap B again the solid sticks of phosphorus may be removed from the glass tubes by taking hold of the piece of projecting phosphorus, the phosphorus being immediately immersed under water in the tank C, and kept there protected from the action of the light. While, according to Seubert, it would be possible for a workman to mould in an hour's time 30 to 40 kilos. of phosphorus, Fleck has found that, under the most favourable conditions of temperature, it takes six hours to mould 50 kilos. of phosphorus. If it is desired to prepare granulated phosphorus with this apparatus, a stratum of 6 to 8 centimetres thickness of hot water is so carefully poured on cold water as not to mix ; next the tap, B, is opened sufficiently to cause the phosphorus to form drops, which, immediately on falling into the cold water, becomes a hard solid mass. For practical purposes granulated phosphorus is preferable to the moulded sticks. The phosphorus is stored either in strong sheet-iron tanks or in wooden boxes lined with thinner (tinned) sheet-iron, these vessels being capable of holding 6 cwts. of phosphorus covered with a stratum of water fully 3 centimetres deep. When large quantities, say, from 1 to 5 cwts., of phosphorus have to be sent off, it is usually packed in water in small wine casks, and the casks having been tightly closed, are coated externally with molted pitch, then rolled through chaff, and lastly covered with stout canvas sewed tightly round the cask. Another method of packing phosphorus consists in placing it in well-made water-tight sheet-iron or tinned iron canisters, such as are largely used in London for the purpose more particularly of conveying oil paints, and which are closed by soldering on a lid very securely. In some cases these canisters are packed in wooden boxes to the number of six or twelve, according to size and weight.

The process for obtaining phosphorus proposed by Fleck depends on the solubility of calcium phosphate in hydrochloric acid and its separation as acid calcium phosphate on evaporating down the solution in stoneware vessels. According to theory 156 parts calcium triphosphate $Ca_3(PO_4)_2$ require 73 parts anhydrous hydrochloric acid, yielding 111 parts calcium chloride, 100 parts acid calcium phosphate, and 18 parts of water. On igniting 100 parts acid calcium phosphate and 20 parts carbon there are formed 21·3 parts phosphorus, 5·2 parts calcium triphosphate, and 46·7 parts carbon monoxide. If the residual mixture of calcium triphosphate and carbon is incinerated and again treated with hydrochloric acid, calcium phosphate is again obtained from the solution on evaporation and so on. It is thus possible to extract in this manner all the phosphorus from the bones if the acid is free from sulphuric acid. The bones, cleansed, broken up and freed from fat, are treated with dilute hydrochloric acid at 10° Tw. The bones are then laid in hydrochloric acid at 5° Tw., in which they are left until completely softened; this second liquid serves instead of water for mixing the acid for the lixiviation of fresh bones. When the first liquid, a solution of acid calcium phosphate and calcium chloride, marks 24° Tw., it is placed in the evaporating vessels.

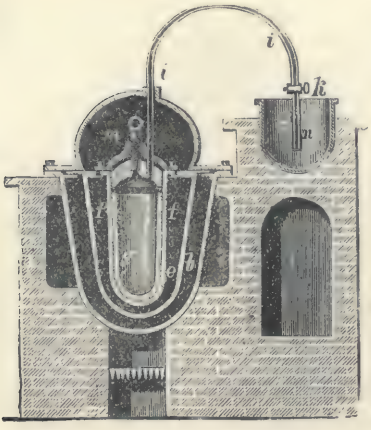
In the choice of these vessels lies one of the difficulties of the Fleck process, as hydrochloric solutions cannot be evaporated in leaden vessels, but require the use of stoneware vessels, not easy to be procured. The lye crystallises when it reaches 50° Tw. The crystalline paste is pressed and mixed with one-fourth its weight of charcoal powder in an earthen pan at 100° and rubbed through a copper sieve. The crude phosphorus

obtained is refined and moulded as usual. The residue of calcium phosphate and carbon is incinerated and lixiviated with strong hydrochloric acid. The bones which have been freed from calcium phosphate are worked up for glue.

Properties of Phosphorus.—When perfectly pure and kept under distilled water, which previously to being employed for this purpose has been by boiling deprived of the air it held in solution, and has been cooled either under a layer of oil or in well-stoppered bottles, and in perfect darkness, phosphorus is a colourless and transparent substance; but usually it has a white-yellow colour and waxy appearance. Its sp. gr. is = 1·3 to 1·84. When the temperature of the air is not too low this element is as soft as wax, but becomes brittle in cold weather. Phosphorus cannot be pulverised; is tough; but when molten in a bottle under warm water and shaken until the fluid is quite cold the substance is thereby reduced to a finely divided state; instead of water it is better to use either alcohol, urine, or a weak aqueous solution of urea. Phosphorus fuses at 44° to 45°, and remains, especially if kept under an alkaline solution, fluid for a considerable time though cooled far below its melting-point, but solidifies suddenly when touched by a solid body. At 290° phosphorus boils, and it evaporates sensibly at the ordinary temperature of the air. By slow oxidation (fumes of phosphorus are given off at the ordinary temperature of the air) there is formed not only phosphorus acid but nitrate of ammonia and antozone. Phosphorus is in the state of vapour slightly soluble in water. The solid element itself is slightly soluble in alcohol and ether, also in linseed oil and oil of turpentine, the best solvents being sulphide of carbon, chloride of sulphur, and chloride of phosphorus. At 75° phosphorus ignites in contact with air, and in order to ignite it by friction this temperature has to be reached. Amorphous or red phosphorus requires a very high temperature (300°) for ignition. Commercial phosphorus usually contains some impurities, such as sulphur, arsenic, and sometimes traces of calcium, due to the lime of the bone-ash used in the preparation. Beside being used in chemistry, phosphorus is chiefly employed in the making of matches; also for what is termed liquid fire (a solution of phosphorus in sulphide of carbon), for the preparation of tar colours, and for hardening some copper alloys.

Amorphous or Red Phosphorus.—Dr. Schrötter, of Vienna, discovered in 1848 that the property possessed by ordinary phosphorus (first noticed in 1844 by E. Kopp) of becoming coloured red by the action of light, was due to the formation of an allotropic modification, which has been since termed red or amorphous phosphorus. This is best prepared by heating ordinary phosphorus, with exclusion of air and water, in a closed vessel and under pressure, to 250° for a length of time. On the large scale this operation is conducted in an apparatus invented by A. Albright, of Birmingham. In Fig. 358, *g* represents a glass or porcelain vessel, filled for five-sixths of its capacity with pieces of phosphorus to be heated to 230° to 250°. The vessel, *f*, is placed in a sand-bath, *b*, heated by the fire. To the vessel, *g*, is fitted an air-tight lid, into which is fastened the bent tube, *i*, provided with a tap, *k*, and dipping into the vessel, *n*, which is filled with water, or preferably with mercury covered with a layer of water. The tap, *k*, is left open at the commencement of the operation for securing the escape of the air contained in *g*, and as soon as no more air escapes the tap is closed, and the heat increased so as to convert the ordinary into amorphous

Fig. 358.



phosphorus. The time required for the operation depends upon conditions which can be met only by experience. After the thorough cooling of the apparatus, the vessel, *g*, is opened, and the red phosphorus removed. It is then placed under water and crushed to a pulp in order to remove any unconverted ordinary phosphorus. Carbon disulphide might be used for this purpose, but the danger of ignition (by accident) of the solution of ordinary phosphorus thus obtained is prohibitive. Nicklès proposes to separate ordinary from amorphous phosphorus by shaking up the mixture of amorphous and ordinary phosphorus with a fluid, the specific gravity of which is less than that of amorphous phosphorus (2·1), and greater than that of ordinary phosphorus (1·84). A solution of calcium chloride at 66° to 71° Tw. can be used for this purpose; the ordinary phosphorus floats in this fluid and can then be readily taken up by carbon disulphide, while the operation can be carried on in a closed vessel. When very large quantities of amorphous phosphorus have to be purified it is best to follow Coignet's plan, consisting in treating the boiling mixture of the two varieties of phosphorus with caustic soda solution, whereby the ordinary phosphorus is converted into phosphuretted hydrogen gas, and sodium hypophosphite formed, the remaining amorphous phosphorus being purified by washing with water. R. Böttger suggests the use of a solution of copper sulphate, which with ordinary phosphorus forms copper phosphide.

Properties of Amorphous Phosphorus.—This substance occurs either in powder of a red or scarlet colour or in lumps of a red-brown hue; fracture conchoidal, sometimes with an iron-black hue; sp. gr. = 2·1. Amorphous phosphorus is not soluble in carbon disulphide or other solvents of ordinary phosphorus. It is unaltered by exposure to air; and when heated to 290° is re-converted into ordinary phosphorus. When mixed and rubbed with dry potassium bichromate, red phosphorus does not explode, and when mixed with nitre it does not burn off by friction, but only by application of heat, and then noiselessly. It explodes, however, when mixed with potassium chlorate. With lead peroxide, amorphous phosphorus ignites by friction with a slight explosion, but when heat is also applied a violent explosion ensues.

Owing to its properties and behaviour with several oxides, its non-volatility and non-poisonous properties, as well as on account of its less ready ignition, amorphous phosphorus is an excellent material for the making of matches; but amorphous phosphorus is not in general use for this purpose. It is, however, used for preparing phosphorus iodide, which serves for the preparation of iodides of amyl, ethyl, and methyl, used in the manufacture of cyanin, ethyl violet, and other coal-tar colours. Sir William Armstrong's explosive mixture for shells contains amorphous phosphorus and potassium chlorate. From 66,000 cwts. of bones there are annually prepared in Europe some 5500 cwts. of phosphorus.

The production of phosphorus in 1880 was approximately as follows:—

England (Albright & Wilson at Oldbury, near Birmingham)	1750 tons
France (Coignet Frères, at Lyons)	1500 „
Philadelphia	18 „

There is a phosphorus factory in Sweden, but its output is not known. The yearly consumption of phosphorus in Germany is estimated at 1200 tons.

MATCHES: PRODUCTION OF FIRE.

In the year 1823, Döbereiner, at Jena, discovered that finely divided spongy platinum has the property of igniting a mixture of atmospheric air and hydrogen gas, and he contrived the so-called Döbereiner hydrogen lamp, which has been, and is still occasionally, employed to procure fire and light. About the same period there was invented a kind of phosphorus match of the following arrangement:—Equal parts of

sulphur and phosphorus were cautiously fused in a glass tube; after the fusion was completed the tube was tightly corked. If it were desired to obtain fire, a thin splint of wood was immersed in this mixture, and some of it having been fixed to the wood, the latter on being brought into the air became ignited by the combustion of the mixed substances, which took fire spontaneously in the air. It is evident that this rather clumsy contrivance never became general. Of far more importance as suited for practical purposes were the chemical matches or dip splints, first manufactured at Vienna, as early as 1812. These splints were tipped with sulphur covered with a mixture of potassium chlorate and sugar, to which for the purpose of imparting colour was added some vermilion, while a little glue gave a pasty and adhesive consistency. By touching this composition with concentrated sulphuric acid ignition ensued; the acid was kept in a small glass or leaden bottle into which some asbestos had been inserted, which acted as a sponge for the acid. The only friction matches known up to the year 1844 were discovered and made by M. Chancel, assistant to the well-known Professor Thénard of Paris, 1805. The "Prometheans," first made in England in or about the year 1830, were contrived on the same principle, viz., the ignition, by friction between two hard substances, of a mixture of potassium chlorate and sugar fixed to a kind of paper cigarette, which contained also a small glass globule filled with sulphuric acid; however, the high price of this kind of match prevented its general use. Under the name of "Congreves" the first real friction matches were made in 1832. On the sulphur-tipped splints was glued a small quantity of a mixture of one part of potassium chlorate and two parts of black antimony sulphide, to which some gum or glue was added. By strongly rubbing this composition between two pieces of sand-paper the mixture became ignited, but frequently also, on becoming detached from the wooden splint, flew about in all directions without igniting the sulphur or the wood. It is not well known who was the first to substitute phosphorus for antimony sulphide; but according to Nicklès, phosphorus matches were already used in Paris as early as 1805, while in 1809 Derépas proposed to mix magnesia with phosphorus in order to lessen its great inflammability when in a finely divided state. Derosne (1816) appears to have been the first who made phosphorus friction matches at Paris. However, it was not before the middle of 1833 that phosphorus matches became more generally known, when Preshel, at Vienna (a city famous for the match and fusee industry), made not only phosphorus matches, but also fusees and German tinder slips tipped with the phosphorus composition. About the same period F. Moldenhauer, at Darmstadt, made phosphorus lucifer matches. The South Germans attribute to Kammerer the invention of phosphorus lucifer matches, while in England, according to the opinion of the late celebrated Faraday, John Walker, of Stockton, Durham, was the inventor of lucifer matches, or at least the first maker. The older kind of matches, although very combustible, ignited with a rather sharp report, owing to the presence of chlorate of potash in the mixture, while, moreover, the too ready ignition by concussion rendered the carriage of these matches so unsafe that in Germany the transport, as well as the manufacture, became prohibited. In the year 1835 Trevany substituted a mixture of red lead and manganese for a portion of the chlorate of potash, thereby greatly improving the composition. In 1837 Preshel altogether discarded this salt, substituting peroxide of lead, or, as Böttger advised, either a mixture of red lead and potassium nitrate, or of lead peroxide and nitrate. From this period the manufacture of matches became an extensive industry, greatly aided by the manufacture of phosphorus on the large scale.

In the course of time other improvements were made, as, for instance, the substitution for sulphur of wooden splints, thoroughly dried and soaked in wax, paraffine, or stearic acid, and the coating of the composition with a varnish to protect it from the action of moisture, while, at the same time, the appearance of the matches was

rendered more ornamental. At the present day matches are the product of an industry which cannot possibly be much more improved in a technical point of view, besides being, as regards price, within the reach of all.

However useful phosphorus lucifer matches may be, it is a great drawback to their utility that the combustible composition is a poisonous mixture; while, moreover, the workpeople engaged in that department of the lucifer-match making in which the phosphorus is handled are often affected by a peculiar kind of caries of the jawbones, the real cause of which is the more difficult to ascertain as the workpeople engaged in the manufacture of phosphorus, and exposed to its vapours to such an extent as to render their breath luminous in the dark, are not similarly affected. The discovery of the red or amorphous phosphorus, which is neither poisonous nor very inflammable, affords a happy substitute for the ordinary phosphorus, but the former is by no means generally used in the preparation of matches.

Manufacture of Lucifer Matches.—The operations required are:

1. The preparing of the splints of wood.
2. The mixing of the combustible composition.
3. The dipping, drying, and packing of the matches.

1. *The Preparation of the Wooden Splints.*—Generally white woods are used for this purpose, such as white fir, pine, aspen, more rarely fir (*Föhrenholz*), sometimes beech, lime-tree, birch, willow, poplar, and cedar. The shape of the splints is usually square in section, but abroad the splints are sometimes cylindrical. The square splints are readily made by hand, simply by splitting up a block of wood of the length required for the splint. A cutting tool, a large knife, similar to that which is sometimes used by chaff-cutters, is very frequently used for the purpose of cutting the wooden splints, while a contrivance similar to that in use for propelling the hay or straw forward is also employed, being so arranged as, after every cutting stroke, to propel the wood the length required for a splint. More generally the operation of splitting the block of wood parallel to its fibres and next cutting off the splints to the required length is effected by machinery, consisting of fixed knives, against which the wood is moved with sufficient force to split it up into splints, which are next cut to the required length. Instead of splitting the wood by these means, the splints are now in Germany always made by a kind of plane, invented by S. Römer, of Vienna, by which the wood is cut into circular splints. The cutter of this plane differs from that of the ordinary carpenter's plane in possessing, instead of the cutting edge, a slight bend, in which three to five holes have been bored in such a manner that one of the edges of these holes is sharpened; in practice, three holes are preferred. When this plane is forced against a lath of wood, placed edgeway, the cutting tool penetrates into the wood, splitting it up into as many small sticks or splints as the cutter contains holes. When a number of thin splints have been cut from the lath, it is again planed true with an ordinary plane and then the operation repeated. The dividing of the thin sticks into splints of the required length is effected by a tool consisting of a narrow trough about 6 centimetres wide and provided with a slit in which works a knife fastened to a lever. A clever workman can prepare 400,000 to 450,000 splints daily. In the south-west of Germany a plane for cutting wooden splints, the invention of Anthon, at Darmstadt, and similar in action and construction to that above mentioned, is in general use; but throughout an extensive portion of the empire the manufacture of the splints has become a separate trade, often carried on in woods and forests, the splints being sold to the lucifer-match makers in bundles ready for dipping.

Instead of making the splints by hand, they are occasionally made by a machine, such as that of Pelletier, at Paris (1820), having on a bench a plane 36 centimetres long by 9 wide, made to move backwards and forwards, while a piece of wood is placed

so that it is caught by the fore-cutter, which consists of a steel knife provided with twenty-four teeth sharpened like little knives, the second cutter removing the small laths from the plank of wood. Cochot's machine (1830) consists of a large iron wheel 1 metre in diameter, on the periphery of which are fixed thirty wooden blocks lengthways of the size of the splints. When the wheel is turned round, the blocks of wood are caught by the knives fastened to a small cylinder, and the wood is split up into splints, which are removed from the block by another knife. Jeunot's machine, patented in 1840 in France, is of a similar construction. Neukrantz, at Berlin (1845), contrived a tool based upon the principle of the hand-plane, the wood intended to be cut being moved against a fixed steel cutter, which produced sixteen to twenty splints at a movement. Krutzsch, at Wünschendorf, Saxony, has improved upon this plan (1848) by perforating a steel plate with about 400 holes placed as near together as possible; the edges of these holes having been sharpened, a block of wood is forced in the direction of its fibres against the plate and thus divided into splints. A piece of wood 3 centimetres in thickness and width by 1 metre in length yields 400 lengths, each of which can be cut up into fifteen splints; 6000 of the latter are made in two minutes. Of the several tools and machines contrived for the purpose of cutting splints—and the number of these contrivances is very large—we quote the following of German origin. The machine invented by C. Leitherer, at Bamberg (1851), consists of what might be termed a kind of guillotine, viz., a box at the bottom of which is placed the wood to be formed into splints, the fibre of the wood being vertical. In front of this box is placed a framework, in which a heavy block, provided with four cutters, each terminated by eight to ten narrow tubes (somewhat similar to cork-borers), can be made to move rapidly, so as to give forty-five strokes a minute, the wooden block intended to be cut into splints being made to move under the cutting tool after each stroke. Wrana's machine is in principle the same as that of Neukrantz, but has been greatly improved, the plane not being fixed, but supported by a piece of wood. Long's machine, again, consists of a series of cylinders, between which the block of wood is placed, while knives are so arranged as to cut the block into splints while the wood moves on by the motion imparted to the cylinders.

2. *The Preparation of the Combustible Composition* is carried on in the following manner:—The glue, or gum, or any other similar substance is first dissolved in a small quantity of water to the consistency of a thin syrup, with which, having been heated to 50°, the phosphorus is incorporated by gradually adding it and keeping the mixture stirred so as to form an emulsion, to which are next added the other ingredients after having been pulverised. In order to obtain a good composition, it is essential that there should be neither too much nor too little phosphorus, for an excess of phosphorus will not only tend to increase unnecessarily the price of the composition, but it has also the effect of rendering it unfit for igniting the sulphur and stearin wherewith the matches are tipped, because the phosphoric acid generated by the combustion of the phosphorus is deposited as an enamel-like mass, which prevents further combustion. It appears that the best proportion is from one-tenth to one-twelfth of phosphorus.

A much smaller quantity of phosphorus is required if this element is first dissolved in carbon disulphide and the solution added to the other constituent of the composition; the carbon disulphide while rapidly volatilising leaves the phosphorus in a very finely divided state. As phosphorus is very readily soluble in sulphide of carbon, and as the latter is moderately cheap, the method has the advantage that the mixing of the materials can take place without the application of heat. It is, however, evident that the greatest care is required in manipulating such a liquid as sulphide of carbon, and far more when phosphorus is dissolved therein. C. Puscher suggested (1860) the use of phosphorus sulphide, P_2S, instead of pure phosphorus in the composition for

matches. He prepared a composition containing 3·5 per cent. of this sulphuret, and obtained excellent matches.

Among the metallic oxides which are employed in the mixture, preference is given either to a mixture of lead peroxide and potassium nitrate, or to a mixture of the former with lead nitrate obtained by treating red lead with a small quantity of nitric acid and leaving this mixture for a period of several weeks to dry. Glue, gum, and dextrine are used as excipients; the first, however, is objectionable because it carbonises and prevents the combustion. Perhaps a dilute collodion solution or a mixture of sandarac or similar resin, with benzole, might be used as an excipient instead of the gum.

The mixtures actually used in the trade are kept secret, but the following recipes may give some idea of the composition :—

I.

Phosphorus	1·5 parts	
Gum senegal	3·0 ,,	
Lamp-black	0·3 ,,	
Red lead	5·0 ,,	A mixture of lead nitrate and peroxide, technically known as oxidised red lead.
Nitric acid, sp. gr. 1·384	2·0 ,,	

II.

Phosphorus	8·0 parts	Dissolved in the required quantity of carbon disulphide.
Glue	21·0 ,,	
Lead peroxide	24·4 ,,	
Potassium nitrate	24·0 ,,	

III.

Phosphorus	3·0 parts
Gum senegal	3·0 ,,
Lead peroxide	2·0 ,,
Fine sand and smalt	2·0 ,,

No doubt there is room for great improvements in these compositions.

3. *Dipping and Drying the Splints.*—In order to fix the sulphur and combustible composition to one end of the splints, it is clear that these should not touch each other, but be so arranged as to leave an intermediate space. A contrivance is employed, consisting of small planks, 0·3 metre long by 10 centimetres wide, the surface being provided with narrow grooves placed both together, and just large enough each to hold a single splint, Fig. 359. The splints are one by one placed in the grooves, an operation usually performed by girls. One plank having been filled another is placed

Fig. 359.



Fig. 360.



Fig. 361.



on the top of it. The surface of the plank on one side is provided with a piece of coarse flannel, while the other side is grooved for holding splints. Each of the planks has at the end a round hole, through which pass iron rods, Figs. 360 and 361, in the

top of which a screw thread is cut, so that as soon as some twenty to twenty-five planks have been filled with splints and placed one upon another, they are fastened so as to form a framework. A clever hand can fill during ten hours fifteen to twenty-five of these frames, each containing 2500 splints. Attempts have lately been made to perform this work by machinery, and the machine constructed by O. Walsh, at Paris (1861), enables a lad to frame 500,000 to 600,000 splints in ten hours.

The sulphur intended for dipping the splints is kept in a molten state over a moderate fire in a shallow rectangular trough, in the middle of which a stone is placed as precisely level as possible. The quantity of sulphur is so regulated that it covers the stone to a depth of 1 centimetre. In the operation of dipping, the ends of the splints are made to just touch the stone and immediately removed, care being taken to cause, by shaking the frame, any superfluous sulphur to flow into the trough again.

In the dipping apparatus of Roller the mixture is in the cast-iron pan, *a* (Figs. 362, 363, and 364). In its middle there is a dipping plate, *b*, in two ribs, *c*, upon which the ignition mass is spread in the usual manner. Into this stratum of uniform thickness the woods, previously fixed in the frame, *z*, are dipped with the end to be coated. In order to dip all the splints equally deep, even if they have been laid unevenly, the

Fig. 362.

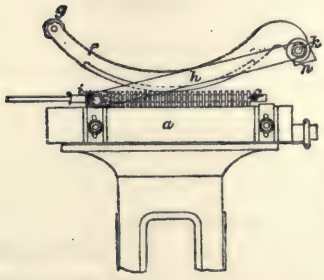


Fig. 363.

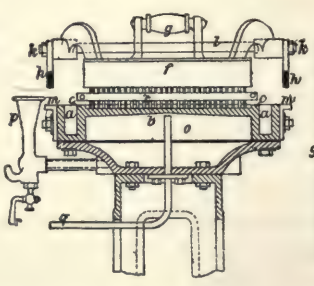
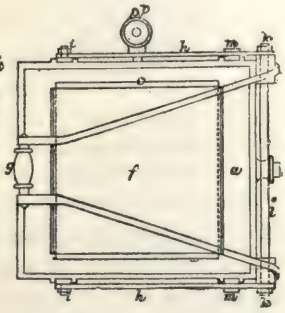


Fig. 364.



press plate, *f*, is held by its handle, *g*, and rolled over the filled frame. The weight of *f* pushes down any splints which stand up above the level and presses all down to the planed surface of the dipping plate, *b*. For guiding the press plate, *f*, there serve the two counter-guides, *h*, which turn on the pivot, *i*, and the joint, *k*, in a curve approaching to a cycloid.

When at rest the press plate, *f*, stands perpendicularly behind the dipping table, whilst the counter-guides, *h*, come in contact with the angles, *m*, the press plate, *f*, turns on the connecting bolt, *l*, and the pieces, *n*, are supported against the side of the pan. The hollow space, *o*, of the dipping pan, closed below by the foot, serves for warming the ignition mass, if needful, by hot water, steam, or hot air. The funnel, *p*, serves for introducing hot water or letting off that which has become cold through the cock, *r*.

Inodorous matches, when dry, are coated with a coloured solution of resin, or sometimes finally with collodion. Phosphorus is recovered from matches which adhere together by boiling in water.

Matches with Amorphous Phosphorus.—This variety of match was invented in 1848 by Böttger, at Frankfort, and was prepared industrially by Fürth, at Schüttenhofen; Lundström, at Jönköping (Sweden); Coignet, at Paris (under the name of *Allumettes hygiéniques et de sûreté au phosphore amorphe*); De Villiers and Dalemagne, Paris (under the name of *Allumettes androgynes*); also by Förster and Wara. These matches are of two kinds: (*α*) Those which are free from phosphorus, the amorphous phosphorus being incorporated with the sand-paper; (*β*) Those which are free from phosphorus both in the match and on the sand-paper.

To the matches of the first category belong: (1) Matches the composition of which is free from phosphorus, consisting simply of a pasty mass, the main constituents of which are antimony sulphide and potassium chlorate. (2) The amorphous phosphorus, mixed with some very fine sand or other substance promoting friction, is, with glue, put on to the box in which the matches are contained; or, as is the case with the *androgynes*, at the other end of the splint. The friction surface on the boxes consists of a mixture of 9 parts of amorphous phosphorus, 7 parts of pulverised pyrites, 3 parts of glass, and 1 part of glue. The matches ignite readily by friction on the surface containing this composition, but do not ignite when rubbed on any other rough surface. These so-called safety matches are largely manufactured at Jönköping, under the Swedish name of *Sakerhets-Tändstickor* (security fire matches). Jettel (1870) uses for the friction surface a compound consisting of equal parts of amorphous phosphorus, pyrites, and black antimony sulphide; for coating on the two sides of 1000 small boxes, each containing fifty matches, about 80 grammes of this mixture are required. It need hardly be mentioned that in England safety matches are largely made and of excellent quality.

B. Förster and F. Wara, at Vienna, have introduced a "non-poisonous" match. The amorphous phosphorus is mixed up with the combustible composition in the usual way, so that these matches ignite readily by being rubbed on any rough surface, but the ignition is accompanied by noise, owing to the potassium chlorate contained in the mass.

As regards the matches belonging to the second category—viz., such as neither contain phosphorus nor require a phosphorus-containing surface, we may give the analysis, by Wiederhold, of the composition of those made by Kummer and Günther, at Königswalde, near Annaberg, in Saxony:

Potassium chlorate	8 parts
Black antimony sulphide	8 „
Oxidised red lead	8 „
Gum senegal	1 „

Oxidised red lead is a variable mixture of lead peroxide, nitrate, and undecomposed red lead. Wiederhold, at Cassel, suggested (1861) the following ignition mixture:—

Potassium chlorate	7·8 parts
Lead hyposulphite	2·6 „
Gum arabic	1·0 „

This is the best anti-phosphorus mixture. Jettel, at Gleiwitz, gives the following mixtures free from phosphorus:—

	a.	*b.*	*c.*	*d.*
Potassium chlorate	4·0	7·0	3·00	8·0
Sulphur	1·0	1·0	—	—
Potassium bichromate	0·4	2·0	—	0·5
Antimony sulphide	—	—	—	8·0
Sulphur auratum, SbS_5 (Stibium sulphuratum aurantiacum) (Antimonium sulphuratum, B.P.)	—	—	0·25	—
Lead nitrate	—	2·0	—	—

While R. Peltzer has called attention to the applicability of copper-sodium hyposulphite for the preparation of a phosphorus-free ignition mass, Fleck* has also remarked the use which might be made of sodium in this respect.

Wax or Vesta Matches.—Instead of the phosphorus composition being fixed to a wooden splint, in the wax matches (*allumettes bougies*) it is attached to a thin taper made of a few cotton threads (four to six) immersed in a molten mixture of 2 parts of

* *Jahresbericht der Chem. Technologie* (Dr. Wagner), 1868, p. 220.

stearine and 1 part of wax or paraffine. The tapers, while this mixture is hot, are drawn through a hole perforated in an iron plate, the opening of which corresponds to the desired thickness of the taper. The taper is next cut, by means of machinery, into suitable lengths; afterwards the phosphorus composition is affixed and the vestas put into boxes.

Zulzer's machine for cutting the tapers and for making them into matches has the following arrangement:—The wicks, having been rolled on a drum, are forced between two cylinders, which impart the fatty composition, and next the tapers are carried by the machinery across grooves in planks to holes in a movable vertical iron plate, which is connected with a cutting apparatus intended to divide the tapers into suitable lengths. As the cutters are placed at the entrance of the holes, the tapers, after having been separated from the main wicks, are left dangling in those holes, and, by a mechanical contrivance, the plate containing the holes is lifted sufficiently to bring another row of holes level with the wick-producing apparatus. When a plate has been thus filled with tapers it is removed, another put in its place, and the ends of the tapers immediately immersed in the phosphorus composition, and next placed in a drying room. Marseilles is the great centre of the wax-match industry, while Austria stands next.

PHOSPHATES, MANURES.

Since Liebig demonstrated the importance of phosphoric acid, of nitrogen (as nitric acid and ammonia), and of potash as plant-food, so-called artificial manures have come more and more into use in agriculture.

Poudrette.—Repeated attempts have been made to bring the contents of cesspools, &c., into a portable condition. But as the cesspools contain in the mean 96 per cent. of water and only 0·35 per cent. of nitrogen, with 0·2 per cent. of phosphoric acid, the attempt seems vain. However, a manure obtained by precipitating sewage contains, according to Tidy, 3 per cent. ammonia and 5 per cent. tricalcium phosphate derived exclusively from the sewage. So that irrigation is not the only method of utilising human excreta, though in dry, hot climates it may be the best.*

Guano.—On certain islands off the Peruvian coast the droppings of sea-fowl had accumulated to a depth of 60 metres. In 1853 the quantity of these deposits was estimated at 12 million tons, but they are now nearly exhausted.

Guano contains:

	I.		II.		III.
Sal-ammoniac	2·25	...	6·500	...	4·2
Ammonium urate	12·20	...	3·244	...	9·0
„ oxalate	17·73	...	13·351	...	10·6
„ phosphate	6·90	...	6·250	...	6·0
„ carbonate	0·80	...	—	...	—
„ bromate	1·06	...	—	...	—
„ magnesium phosphate	11·63	...	4·196	...	2·6
Sodium phosphate	—	...	5·291	...	—
Calcium phosphate	20·16	...	9·940	...	14·3
„ oxalate	1·30	...	16·360	...	7·0
„ carbonate	1·65	...	—	...	—
Sodium chloride	0·40	...	0·100	...	—
Potassium sulphate	4·00	...	4·227	...	5·5
Sodium sulphate	4·92	...	1·119	...	3·8
Waxy matter	0·75	...	0·600	...	—
Sand and clay	1·68	...	5·904	...	4·7
Water	4·31	...	22·718	...	32·3
Organic matter	8·26				
	100·00		100·000		100·0

* Compare Slater, *Sewage Treatment*, 1888.

A more recent analysis gave:

	Per cent.	
$Ca_3P_2O_8$	31·759	P_2O_5 = 15·552 per cent.
$Mg_2P_2O_7$	1·568	
$MgSO_4$	0·838	
$CaSO_4$	10·113	
$CaCO_3$	1·612	
NaCl	7·238	
Fe_2O_3, Al_2O_3	0·598	
Insoluble	3·840	
Water	16·175	
$C_5H_3(NH_4)N_4O_3$	3·122	
NH_4NO_3	1·499	
$(NH_4)_2CO_3$	2·823	
Organic matter	13·815 = 2·513 N = 3·052 NH_3	
	100·000 = 5·075 total N = 6·163 NH_3	

Guano from Mejillones contains about 70 per cent. tricalcium phosphate and only 0·3 to 0·8 per cent. nitrogen. Guano from the Aves Islands, on the coast of Venezuela, contains 45 to 50 per cent. of phosphate and 0·3 to 0·4 per cent. nitrogen. Guano from Sydney Island contains 34 per cent. phosphoric acid and 0·28 per cent. nitrogen; that from Cape Verde, 11 per cent. phosphoric acid and 0·3 nitrogen.

Guano is used powdered and sifted, but generally rendered soluble by admixture with sulphuric acid (chamber acid) to get the phosphoric acid into solution. The pasty mass solidifies on cooling from the formation of gypsum, and is therefore again pulverised and sifted.

Bone Meal.—The bones are deprived of fatty matter and ground finely. Various samples of bone meal had the following compositions:

	I.	II.	III.
Bone earth	63·3	60·7	47·7
(Containing phosphoric acid)	25·5	25·4	20·0
Organic matter	29·7	31·8	42·5
Nitrogen	3·9	3·5	4·7
Water	3·9	5·0	7·4
Sand	3·1	2·5	2·4

Precipitated Tricalcium Phosphate can scarcely be produced to advantage at the present prices for hydrochloric acid.

Superphosphate.—To render soluble the phosphoric acid present in natural phosphates, they are mixed with sulphuric acid—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$*

Monocalcium phosphate is freely soluble in water, whilst tricalcium phosphate, $Ca_3P_2O_8$, is sparingly soluble.

The most important materials for the manufacture of superphosphate are the phosphorites. That occurring in large masses in Estremadura is nearly pure phosphate, but large quantities are met with in commerce which contain only 60 per cent. along with considerable quantities of silica and calcium chloride.† Of less value are the staffelites from the valley of the Lahn.

The Canadian phosphorite contains:

Tricalcium phosphate	91·20
Calcium fluoride	7·60
„ chloride	0·78
Sand	0·90
	100·58

* Compare Griffith: *Treatise on Manures*, p. 146.

† And occasionally calcium fluorides.

South Carolina phosphate contains:

Moisture	7·79
Organic matter	4·60
Silica	10·35
Calcium carbonate	8·20
Tricalcium phosphate	61·89
Earthy and alkaline salts	7·17
	100·00

Coprolites, the fossil excrements of saurians, are found in the lias at Norfolk, Suffolk, Cambridgeshire, &c., in England, and near Helmstadt, in Germany.

A sample of Cambridge coprolites contained:

Moisture	0·12
Organic matter and combined water	5·61
Silica	0·18
Carbon dioxide	6·50
Phosphoric acid	30·21
Lime	49·01
Fluorine	3·08
Alkaline salts	5·29
	100·00

In general the proportion of phosphate in coprolites varies from 15 to 70 per cent.,* so that they must be examined before being used for superphosphate. The spent animal charcoal from sugar works is of less value.

The materials are finely ground and mixed with the requisite quantity of sulphuric acid in pits provided with agitators. The mixture is rendered dry by the combination of the calcium sulphate with water ($CaSO_4.2H_2O$), and is then broken up.

Double superphosphate is made by separating the gypsum from the soluble phosphate, when the solution of the latter is evaporated.

The so-called *reversion* of superphosphates (*i.e.*, their return to an insoluble form) is occasioned partly by the formation or presence of aluminium or ferric phosphates, and partly by the action of calcium carbonate. Superphosphates made from the Lahn phosphorites are peculiarly liable to this change.†

From a double superphosphate, I., the quantities given under II. were dissolved out by lixiviation with small quantities of water in a filter, and those under III. by immediate treatment with much water.

	I.	II.	III.
P_2O_5	49·90	47·20	45·80
SO_3	1·20	1·20	1·20
SiO_2	0·50	—	—
CaO	17·24	15·20	14·70
MgO	1·15	1·12	1·11
Fe_2O_3	2·87	1·32	0·66
Al_2O_3	1·38	1·33	1·38
Na_2O	0·40	0·40	0·40
Water	23·52	—	—
Organic	1·53	—	—

An immediate great dilution dissolves out 1·4 per cent. less phosphoric acid than does gradual lixiviation.

* Fragments of wood have been found among coprolites as rich in phosphoric acid as the animal remains.

† The author thinks that the preference given to soluble phosphates is an error which has cost Germany 200,000,000 marks. Foreign phosphorites have been imported and the Lahn phosphorites exported at very low prices.

As nitrogenous manures, in addition to guano and bone-dust, there are ammonium sulphate, nitre, dried blood, horn-dust, and shoddy. Of sources of potash the chief are kainite and potassium chloride.

For determining nitrogen in ammonium sulphate the ammonia is driven off into normal acid by boiling with soda-lye. Saltpetres are examined by means of the nitrometer. Organic nitrogen and total nitrogen in mixed manures are best determined by the Kjeldahl process. The sample is boiled with strong sulphuric acid, to which phenol is added if a nitrate is present. All the nitrogen is thus converted into ammonia, which is distilled off.

For determining the soluble phosphoric acid the following procedure was agreed upon at a meeting of agricultural chemists held on November 30, 1885 :—

Five grammes of the sample are rubbed up with the strong citrate solution and gradually washed into a ½-litre flask. The mixture is filled up to the mark with the dilute solution of citrate, let stand for eighteen hours at the temperature of the room with frequent shaking, and filtered. 50 c.c. of the filtrate are mixed with so much molybdenum solution that not less than 1 c.c. of the solution may come to each milligramme P_2O_5, and so much strong ammonium nitrate (see below) is added as is equal to a quarter the volume of the mixture. After standing twenty minutes in the water-bath and subsequent cooling, the liquid is filtered, the precipitate washed with dilute ammonium nitrate (see below), and rinsed back into the beaker with ammonia at 2·5 per cent. through the perforated filter. The filter is well washed, and to the ammoniacal solution magnesia mixture is added drop by drop, with constant stirring. The whole is filtered after one hour, the precipitate is washed with ammonia at 2 per cent., dried, and ignited.

Preparation of the Solutions.—(1) Strong solution of citrate. 150 grammes citric acid are put in a 1-litre bottle, dissolved in water, and neutralised with ammonia. To the solution are added 10 grammes citric acid, and the liquid is filled up to the mark with water.

(2) Dilute solution of citrate. 1 volume of the foregoing strong solution is mixed with 4 volumes water.

(3) Strong solution ammonium nitrate. 750 grammes ammonium nitrate are dissolved in water, and the solution is diluted to 1 litre.

(4) Dilute ammonium nitrate. 100 grammes ammonium nitrate are dissolved in water, and the solution is made up to 1 litre.

(5) Molybdic solution. 150 grammes ammonium molybdate are dissolved in water, the solution is diluted to 1 litre, and poured into 1 litre nitric acid of sp. gr. 1·2.

(6) Magnesia mixture. 110 grammes pure crystalline magnesium chloride and 140 grammes ammonium chloride are dissolved in 700 c.c. liquid ammonia (at 8 per cent. actual ammonia) and 1300 c.c. of water.

BORIC ACID AND BORAX.

Boric acid occurs native as sassoline, H_3BO_3; in 100 parts—

Anhydrous boric acid, B_2O_3	56·45
Water	43·55
	100·00

and further in the following minerals :—

Boracite, or magnesium borate and chloride with 62·5 per cent. boric acid			
Rhodicite, or calcium borate	„	30 to 45	„ „
Hayescine, tiza, or calcium borate	„	30 to 44	„ „
Hydroboracite	„	47	„ „
Tincal or borax, sodium borate	„	36·53	„ „
Datholite, or boro-silicate	„	18	„ „
Botryolite	„	20·35	„ „
Axinite	„	2 to 6·6	„ „
Tourmaline	„	2 to 11·8	„ „

Boric acid is found also in small quantities in many mineral waters and in sea-water. Larderellite, or ammonium borate, and lagonite, or iron borate, are both found in very small quantities in Tuscany, and are interesting to mineralogists only.

Boric acid is found as sassolin in many volcanic regions, mixed with sulphur, in the hot springs of Sasso, in Tuscany, and also between Volterra and Massa Maritima in the clefts and rents of volcanic formation of rock. Höffer and Mascagni (1776) first mentioned the occurrence of boric acid in the waters subjected, in the clefts of the rock, to the sulphurous exhalations. The little pools formed in these clefts are variously known as *fumacchi*, *fumarole*, *soffioni*, and *mofetti*. The boric acid deposits in some cases cover an extent of six miles. Since 1818 artificial soffioni have been constructed, and the benefit derived by the country from the introduction of the industry is immense. The first artificial lake was situated near Monte Cerboli, and the product was for some time known as larderellite, from the owner's name, Larderel. The production from these works alone amounted in 1839 to 717,333 kilos., and in 1867 to 2,350,000 kilos. The increase has been greatest since 1854, owing to the energy with which Gazzeri and Durval entered upon the construction of the artificial soffioni.

The soil of the natural lakes, or beds of the natural soffioni, are of a slimy formation, and have a peculiar seething movement due to the escape of the sulphurous vapours from the fumaroles or vents. According to Payen, this vapour or steam may be considered as condensible and as non-condensible, the former containing, besides water, calcium, magnesium, and ammonium sulphate, iron chloride, hydrochloric acid, organic substances, a fishy-smelling oil, clay, sand, and a small quantity of boric acid. The non-condensed vapour consisted of—

Carbonic acid	0·5730
Nitrogen	0·3480
Oxygen	0·0657
Sulphuretted hydrogen . . .	0·0133

Payen is of opinion that the vapours contain no boric acid, while C. Schmidt thinks otherwise, as the vapours, when condensed without contact with the water of the soffioni, yield boric acid. The condensed vapours contain 0·1 per cent. boric acid.

Theory of the Formation of the Native Boric Acid.—Dumas and Payen founded an explanation of the formation of volcanic boric acid upon the hypothesis that there exists in the interior of the volcano or beneath the under-crust of the earth a layer of boron sulphide (B_2S_3), which under the action of the mineral waters becomes converted into boric acid and sulphuretted hydrogen. P. Bolley gives the action as similar to that occurring in the formation of sal-ammoniac, a very common mineral in volcanic regions. Professor Becchi, of Florence, found boron nitride (BN) in one of the under-strata, from which he prepared artificially, by means of steam, ammonia and boric acid. Also Warington (1854) and Popp (1870) attributed the appearance of boric acid and ammonia in volcanoes to the decomposition of boron nitride by evaporation. Recently (1862) Becchi has obtained boric acid by the decomposition of calcium borate in a stream of superheated steam.

The Production of Boric Acid.—The most general method of obtaining boric acid is by the evaporation of the water of the natural or artificial soffioni. The water is either naturally or artificially introduced into the natural fumaroles, as these sometimes do not re-supply themselves with sufficient rapidity. As soon as the water has absorbed a considerable quantity of the vapours it is removed and placed in a large mason-work cistern; this cistern is imbedded in the soil near the fumaroles, and the natural heat is sufficient to cause evaporation. The vapours are condensed in a wooden chimney The separated impurities, gypsum, &c., remain in the cistern. As soon as the solution is of a sp. gr. = 1·07 – 1·08 at 80°, it is poured into leaden crystallising vessels, where

the boric acid crystallises out. The mother liquor is evaporated to dryness. It should be remembered that the entire operation is conducted with the assistance of the natural heat of fumaroles only. Occasionally the boric acid is only present in the natural waters to 0·002 of a part ; and in these cases fuel must be used in the evaporation, which therefore entails the expense of carriage, as fuel is very scarce near the soffioni. Charcoal is generally used. But by this means an acid is obtained, containing about 70 to 80 per cent. hydrated boric acid, with 10 per cent. impurities. Clouet removes the impurities by treatment with 5 per cent. of ordinary hydrochloric acid. Boric acid for pharmaceutical purposes may be prepared by dissolving 1 part of borax in 4 parts of boiling water, and decomposing the solution with one-third part of sulphuric, or better with one-half part of hydrochloric acid of 1·2 sp. gr. The acid separates on cooling, and can be purified by crystallisation.

In 100 parts of commercial boric acid from Tuscany, H. Vohl (1866) found:

	1.	2.	3.	4.	5.
Boric acid	45·1996	47·6320	48·2357	45·2487	48·1314
Water of crystallisation	34·8916	35·6983	37·2127	34·9010	38·0610
Water	4·5019	2·5860	1·0237	4·4990	1·5240
Sulphuric acid	9·6135	7·9096	8·4423	9·5833	7·8161
Silicic acid	0·8121	1·2840	0·6000	0·2134	0·0861
Sand	0·2991	0·5000	0·1000	0·7722	0·4154
Iron oxide	0·1266	0·1631	0·0920	0·1030	0·0431
Manganous oxide	0·0031	traces	traces	traces	traces
Alumina	0·5786	0·0802	0·0504	0·1359	0·1736
Lime	0·0109	0·3055	0·1578	traces	traces
Magnesia	0·6080	traces	traces	traces	traces
Potash	0·1801	0·2551	0·5178	0·6140	0·4134
Ammonia	2·9891	3·5165	3·5169	3·7659	3·0890
Soda	0·0029	traces	traces	traces	traces
Sodium chloride	0·1012	0·0595	0·0401	0·1671	0·0321
Organic substances and loss	0·0918	0·0101	0·0101	—	0·0449
	100·0000	100·0000	100·0000	100·0000	100·0000

Properties and Uses of Boric Acid.—Pure boric acid crystallises in mother-of-pearl-like leaves, which at 100° C. lose half their water of crystallisation without melting, the other half being driven off at a red-heat. After cooling, the anhydrous acid appears as a hard, transparent, brittle glass of 1·83 sp. gr. 1 part boric acid dissolves in 25·6 parts water at 15° C., and in 2·9 parts at 100° C. At 8° a saturated solution has a sp. gr. of 1·014. It imparts a green colour to the flame of the spirit-lamp. In a chemical point of view it is similar to silicic acid. Boric acid is largely used in the preparation of borax for glazing porcelain, and, mixed in a weak aqueous solution with sulphuric acid, in the preparation of the wicks of stearine and paraffine candles. It is also used for colouring gold, for decorating iron and steel, in the preparation of flint-glass, and artificial precious stones. In 1859 boric acid was used in the preparation of hydrated oxide of chromium, known under the name of Pannetier's green, *Vert-Guignet*, &c.

Borax.—Borax, or sodium biborate, when anhydrous according to the formula $Na_2B_4O_7$, contains in 100 parts:

Anhydrous boric acid (B_2O_3)	69·05
Soda (Na_2O)	30·95
	100·00

It is found native in Alpine lakes, on the snow-capped mountains of India, China, Persia, in Ceylon, and Great Thibet. It is found in large quantity at Potosi in Bolivia, where the *Borax Lake*, according to Moore's analysis (1870), contains in 1 litre

of its water (sp. gr. = 1·027) 3·96 grammes of borax. Pyramid Lake, Humboldt Co., Nevada, yields also large quantities. By the heat of the sun the water of the borax lakes is evaporated, and the borax crystallises out and is gathered and brought into commerce under the name of tincal. It appears in small six-sided crystals, more or less smooth. The Clear Lake in California, to the north of San Francisco, yields daily 2000 kilos. of borax.

Formerly tincal was purified by washing in water containing soda, to free the borax from adhering fatty substances which combine with the soda to form an almost insoluble soap. After the borax has been well washed, it is dissolved in boiling water; for each 100 parts of refined salts there are added 12 parts of sodium carbonate. The solution is next filtered, and then evaporated to 26° to 30° Tw. It is now placed in wooden crystallising vessels lined with lead, where it is necessary to allow the fluid to cool gradually. Another method is to place the tincal in cold water, and to stir in 1 per cent. of caustic lime. The fatty substances are thus removed, combining with the lime to form an insoluble calcium soap. 2 per cent. of calcium chloride is added to the fluid, which is next evaporated, and set aside to crystallise. Clouet recommends the powdering of the tincal, which is next mixed with 10 per cent. sodium nitrate, and calcined in a cast-iron pan, the fatty substances being thus destroyed. The calcined mass is dissolved in water, and the solution evaporated to crystallisation.

Borax from Boric Acid.—In 1818 the manufacture of borax from boric acid was commenced, and since that time borax has sunk to three-fourths it former price. Both according to the proportion of water and the crystalline form, there may be considered two varieties of borax—(1) the ordinary or prismatic borax; (2) octahedral borax. The prismatic borax ($Na_2B_4O_7 + 10H_2O$) contains in 100 parts:

Boric acid	36·6
Soda	16·2
Water of crystallisation	47·2
	100·0

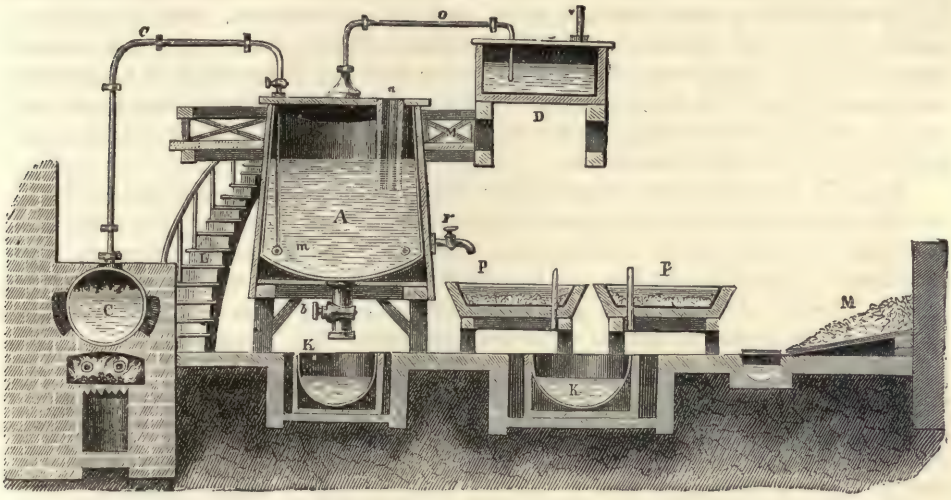
The octahedral borax ($Na_2B_4O_7 + 5H_2O$) contains in 100 parts:

Boric acid Soda	69·36
Water	30·64
	100·00

Prismatic borax is manufactured in the following manner:—There are dissolved in a lead-lined vessel, A, Fig. 365, 26 cwts. of crystallised sodium carbonate in about 1500 litres of water, heated, by means of steam, to the boiling-point. The boiler, C, is for the purpose only of generating steam, which is passed by the pipe, *c*, and the rose, *m*, into A. By means of the large taps, *b* and *r*, the fluid may be removed from A. Through the tube, *a*, the substances thrown down from the solution can be removed. Boric acid is added in quantities of 8 to 10 lbs. after the solution has been heated to the boiling-point. Besides carbonic acid a small quantity of ammonium carbonate is developed, and passes by *o* into the vessel D, containing dilute sulphuric acid, by which it is absorbed. To saturate the solution of 26 cwts. of soda, 24 cwts. of crude boric acid are necessary. The boiling saturated solution marks 32° to 33° Tw., and has a temperature of 104°. If the solution is too strong, water is added; if too weak, a small quantity of crude borax, to bring it to 32° Tw. The solution is allowed to stand in A until all insoluble substances are deposited. The clear lye is conducted by means of the tap, *r*, into the crystallising vessels, P, P, the mud or deposit being received into K. The crystallising vessels are of wood lined with lead. The crystallisation is complete in two to three days, and the mother liquor is drawn off into the vessel H. The

crystals are placed to drain on the inclined plane, M. The mother liquor is retained for the solution of a fresh quantity of soda. After three or four operations, the mother liquor contains sufficient sodium sulphate to admit of profitable crystallisation; and the lye is allowed to cool at 30°. As the solubility of sodium sulphate has reached the

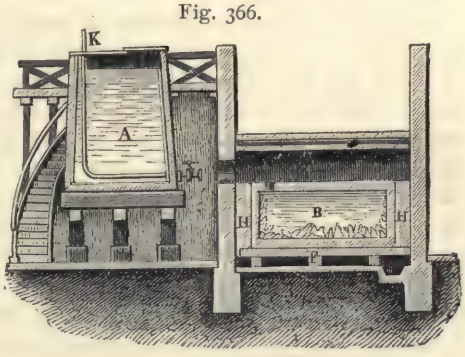
Fig. 365.



maximum at a temperature of 33°, it is clear that the crystallisation of the sulphate commences at the completion of that of the borax. After the crystallisation of the sodium sulphate, the mother liquor is evaporated to dryness, and the saline residue is sold to the glass-manufacturer.

Purifying the Borax.—The crude borax to be purified is placed in a lead-lined wooden cistern, A, Fig. 366, heated by steam. The borax is suspended in a wire sieve immediately under the surface of the water with which A is filled. To 100 parts of borax, 5 parts of crystallised sodium carbonate are added, and the liquid is strengthened from time to time till it marks 33·8° Tw. When the solution has settled it is removed by the tap to the cooler, B. To prevent loss of lye, the floor under B is stippled with waterproof cement, and sloped towards a gutter. The crystallising vessel is of thick timbers, H, F, H, lined stoutly with lead; this vessel is filled with lye to within an inch of the edge, the cover being then placed on. The steam condenses on the cover, which, when removed, is found covered with small crystals, the larger crystals falling to the bottom of the vessel. To hasten the cooling, spaces are left in the timbers, F; but the crystallisation is not effected under sixteen to twenty-eight days. After this time the lye still has a temperature of 27° to 28° C. When quite cool the foreign substances separate from the borax. The vessel, B, contains the large borax crystals from which the adhering mother liquor is separated by a sponge. If the crystals are not thus carefully treated, they split into thin leaves; for this reason also the cooling should be gradual. The crystals are dried on a wooden table, finally sorted, and packed.

Fig. 366.



In England borax is prepared from boric acid in the following manner:—The crude boric acid is mixed with half its weight of calcined soda and submitted to the action of heat in a muffle-oven. The ammonia, which as sulphate is an important constituent of crude boric acid, is, with carbonic acid, given off during the process, and passes through a tube to a condensing chamber. The melted mass is removed, and lixiviated in an iron pan; the suspended matter is allowed to settle, and the clear liquor is put to cool into smaller vessels, in which beautiful crystals form. It has already been mentioned that this manufacture had its origin in France, where sulphuric vapours were employed. A mixture of calcined Glauber salts and boric acid were placed in a retort and subjected to distillation, the residue on lixiviation and crystallisation yielding borax. Köhnke substitutes caustic soda for the sodium carbonate, the borax crystallising from a very alkaline solution.

Recently borax has been obtained from native calcium borate, *tiza*, ulexite, franklandite, or borocalcite (formula, according to Wöhler, $Na_2B_4O_7 + 2CaB_4O_7 + 18H_2O$; or according to more recent determinations, $NaCaB_5O_9.8H_2O$), which occurs in large quantities in California and Nevada, in Greece and Nova Scotia, at Tarapaca in Peru, and in Western Africa. Treatment with sulphuric acid gives only unsatisfactory results, and hydrochloric acid is therefore employed. The acid is poured upon the mineral to two-thirds of its weight with twice the quantity of water, and the whole heated to the boiling-point, and allowed to digest. The heat must be maintained to the completion of the digestion, and the water lost by evaporation re-supplied. The clear liquor is then decanted, and, on cooling, the boracic acid crystallises out, the mother liquor retaining sodium or calcium chloride with a slight excess of hydrochloric acid. Stassfurt boracite, or stassfurtite, is also becoming largely used in the preparation of borax.

Prismatic borax is colourless, and forms transparent crystals of 1·75 sp. gr., soluble in 12 parts cold and 2 parts boiling water, the solution having a weak alkaline reaction upon test-paper, although borax is an acid salt. By exposure to the air it loses water. At a moderate heat it separates into a spongy mass known as calcined borax, and at a red heat assumes a glassy appearance; in this condition it is used as a blowpipe flux.

Octahedral Borax.—Octahedral borax ($Na_2B_4O_7 + 5H_2O$) is prepared in the following manner:—Prismatic borax is dissolved in boiling water till the solution marks 49° Tw. = 1·260 sp. gr. This solution is then allowed to cool very slowly. When the temperature has fallen to 79° C., the octahedral crystals begin to form, the formation continuing till the temperature reaches 56°. After this the mother lye yields only prismatic crystals. Unless great care be taken, a mixed crystallisation results. Buran recommends the preparation of octahedral borax by evaporating a borax solution to 53° Tw. = 1·282 sp. gr., when it is removed to a crystallising vessel. When 10 cwts. of borax are operated upon, the process will take six days to complete. The prismatic and octahedral salt crystallise in distinct layers that can be separated mechanically. Indian borax and Chinese half-refined borax sometimes contain octahedral crystals. Octahedral borax is known in French commerce under the names of calcined borax, jewellers' borax, surface borax, &c. It is distinguished from prismatic borax by its crystalline form and the proportion of water contained, by its sp. gr. = 1·81, and its greater hardness. While the prismatic borax remains unaffected in transparency by exposure to air, the octahedral borax rapidly becomes opaque, and, absorbing five equivalents of water, is converted into the prismatic salt.

Uses of Borax.—The uses of borax are very numerous. Molten borax has the property, at high temperatures, of fluxing metallic oxides, vitrefying with them into coloured transparent glasses; for instance, with cobaltous oxide a blue glass is formed, and with chromic oxide a green glass. This property is of great utility in chemical

analysis, as the various metallic oxides may be thus distinguished in the blowpipe flame. It is also used for soldering metals; and is a constituent of *Strass*, used in glass manufacture and enamelling. It is used extensively in glazing the finer kinds of earthenware, and for separating metals from their ores. Borax forms with shellac in proportion of 1 part to 5 a peculiar varnish, soluble in water, and used when mixed with aniline black to stiffen felt hats. With casein it gives a fluid resembling a solution of gum-arabic, for which it is often substituted. Borax is made into a soap for washing purposes, into a solution for cleansing the hair, and it is also used in various cosmetics, &c. It is largely employed to fix mineral mordants. According to Clouet, a mixture of boric acid and potassium or sodium nitrate is in many cases a better flux than borax. He recommends 100 parts boric acid and 100 parts of the nitrate to be placed in an enamelled iron kettle with 10 per cent. water and heated till fluid. When cooled, flat white crystals are formed; those made with potassium nitrate can be used for crystal-glass manufacture, and those with sodium nitrate for enamelling. Chromium borate is known in commerce as *Vert-Guignet* or Pannetier's green. Borax sold in powder under fanciful names is often adulterated with soda ash, common salt, and even with quicklime.

The Chilian borosodium calcite has the following composition:—

	I.	II.	III.	IV.
Water	27·33	13·8	40·90	31·50
Lime	17·44	15·4	8·38	12·34
Salt	7·19	31·6	14·20	3·80
Insoluble	10·69	10·3	1·04	0·21
Sulphuric acid	12·60	9·4	1·20	trace
Boric acid	22·55	19·6	22·32	47·52
Soda	2·33	—	3·96	1·63

According to the proposal of Lunge, the borate ground and elutriated is mixed with two-thirds its weight of common hydrochloric acid and double the quantity of water, heat being applied until the decomposition is complete. It is now allowed to settle, and the clear hot liquor is drawn off with a syphon. On cooling, the boric acid crystallises out almost entirely, whilst sodium and calcium chloride remain in solution with the excess of hydrochloric acid. The proportion of two-thirds refers to the average composition of the mineral, and must be arranged according to each sample. The crystals of boric acid are drained, pressed, or whizzed, washed in cold water, whizzed again, and obtained almost absolutely pure, so that on treatment with soda they yield pure borax on the first crystallisation.

The bulk of the borax consumed in Germany is prepared from boronite-calcite. The manufacture consists of four processes:

1. Boiling the calcium borate with soda.
2. Working up the residues.
3. Fine crystallisation.
4. Working up the lyes.

The first process is conducted in large pans fitted with powerful agitators, and heated by the direct introduction of steam. 2500 kilos. of the lime salt are stirred up with four to five times its quantity of water, and the soda is gradually introduced when the mixture boils. The soda should be in slight excess. A mixture of soda ash and bicarbonate is preferred. The boiling is completed in three to four hours.

As the neutral borate contains only 4 molecules of crystalline water, the formation of this salt is a serious loss. The contrary condition is also to be avoided. If there is no excess of soda the crystallisation is sluggish. After the whole has settled, the clear supernatant lye is run off and the mud is passed through a filter-press. The lye is kept to crystallise in iron, four-sided cisterns, holding 1000 to 1500 litres. It must have, on the average, a strength of 49°–59° Tw.

In three or four days the crude borax has separated out in thick crystalline crusts on the sides and bottoms of the cisterns. The average pure sodium biborate ($Na_2B_4O_7 + 10H_2O$), contained in these crude crystals is 40 to 50 per cent., the residue being sodium sulphate and chloride. The lyes can be used for boiling several times in succession, but if they become too concentrated it is better to evaporate them down. The first crystallisation obtained on evaporation contains borax enough to be added to the crude borax for further treatment.

The filter press turns out the mud from the boiling in solid cakes, which still contain a quantity of mother liquor. They are lixiviated with hot water; the lye is concentrated and added to the crude borax.

The next stage is the fine crystallisation conducted in large four-sided iron cisterns holding 8–10 cubic metres. They are enclosed with an outer coating of wood, the space between the wood and the iron being packed with sawdust, peat, &c., to prevent sudden changes of temperature.

The crude borax is dissolved in as much pure water as to yield a solution which boiling marks 50° Tw. The so-called fine lye can be repeatedly used for dissolving fresh quantities of crude borax, but the solutions must be made stronger each time, as the sp. gr. is raised by the sodium sulphate, &c.

Care must be taken not to make the solutions too strong. From such lyes octahedral borax crystallises out containing only 5 mols. water of crystallisation, which involves considerable loss, as the prismatic borax—the commercial quality—crystallises with 10 molecules of H_2O.

To remove iron and traces of organic matter a small quantity of sodium hypochlorite is added, until the lye is colourless in water and gives no reaction with potassium ferrocyanide. The hot lye is run into the crystallisation-cisterns, which must be quite full and carefully covered, to prevent too rapid cooling. In ten to fourteen days, according to the weather and the season, the temperature will have fallen to 33°, and the crystallisation of the borax will be completed. At 33° the sodium sulphate begins to crystallise, and the lye must be let off.

The crystalline crusts are rinsed with pure cold water to remove drops of mother liquor, and are then detached by striking the outsides with a hammer. The borax is finally dried in baskets in a drying-chamber at 30° for twenty-four hours, and any dirt adhering to the under side of the crystals is removed.

The lyes from the coarse and the fine crystallisations must not be too often used for repeated boilings, as they would become too rich in sodium sulphate and chloride. Hence large evaporating pans are provided to receive them. In winter after being concentrated they are received into crystallising vats set in the open air, when sodium sulphate crystallises out in quantity. In summer the sulphate and the common salt have to be boiled out, which involves a loss of borax.

In order to recover the borax (about 10 per cent.) which attaches itself to the sodium sulphate, it is heated very gently until the latter salt melts in its own water of crystallisation. The melted sulphate is then run off, and the borax which has remained undissolved remains in hard pieces, which may be added to the fine crystallisation.

Diamond-Boron or Adamantine.—Wöhler and H. Deville in 1857 were the first to notice that boron occurs similarly to carbon in two allotropic conditions, namely, crystalline* and amorphous. Diamond boron is prepared in two ways, either by the reduction of calcined borax with aluminium—

$$\left.\begin{matrix}\text{Boric acid, } B_2O_3,\\ \text{Aluminium, } 2Al\end{matrix}\right\} \text{ yields } \left\{\begin{matrix}\text{Alumina, } Al_2O_3,\\ \text{Boron, } 2B;\end{matrix}\right.$$

or by converting amorphous boron into crystalline. The latter method gives the

* Graphitic boron is by a later discovery of Wöhler's (1867) resolved into boron-aluminium; formula, AlB_2.

better result. 100 grammes of anhydrous boric acid are mixed with 60 grammes of sodium in a small iron crucible heated to a red heat. To this mixture 40 to 50 grammes of common salt are added, and the crucible is luted down. As soon as the reaction is finished, the mass, consisting of amorphous boron with boric acid, borax, and common salt intermingled, is stirred into water acidified with hydrochloric acid. The boron is filtered out, washed with a weak solution of hydrochloric acid, and placed upon a porous stone to dry at the ordinary temperature. Molten iron, it is well known, converts amorphous carbon into crystalline graphitic carbon, and aluminium exercises a similar action upon boron. The crystalline boron is prepared in the following manner:—A small crucible is filled with amorphous boron, in the centre of which a small bar of aluminium weighing 4 to 6 grammes is placed. The crucible is submitted to a temperature sufficient to melt nickel for one-and-a-half to two hours. After cooling, the aluminium will be found covered with beautiful crystals of boron. The diamond-boron is easily separated from the graphitoid. The former is a transparent tetragonal crystal, of a garnet-red or honey-yellow colour, or, if perfectly pure, colourless. It is very brittle, hard, and lustrous; it will scratch rubies easily. This discovery may in time be of great technical importance.

SALTS OF ALUMINIUM.

Alum.—Alum is a saline substance, consisting of aluminium sulphate, potassium, or ammonium sulphate, and water of crystallisation. It occurs native as potash alum and as ammonia alum, being, in fact, a double salt, consisting of either aluminium sulphate and potassium sulphate, or aluminium sulphate and ammonium sulphate. The alum known as potash alum, $\left.\begin{matrix}Al_2\\K_2\end{matrix}\right\}4SO_4 + 24H_2O$, is found in alum-shale. But all natural alums are more of mineralogical than of technical interest, the alums of commerce being always artificially prepared. We shall, therefore, pass on to the consideration of the latter.

Material of Alum Manufacture.—The manufacture of alum is based on the formation of aluminium sulphate and sodium aluminate from the various alum ores. These ores or earths, necessitating different methods of treatment, may be divided into four groups, viz.:—

1. Those which contain alumina, potassa, and sulphuric acid in such proportions that the addition of an alkaline salt is not requisite. To this group belong alum-stone and several varieties of alum-shale.

2. Those in which the aluminium sulphate is alone present, necessitating the addition of alkali salts in large quantities. To this group belong the alum-shale and alum-earths found in the brown-coal formation.

3. Those in which alumina only is contained, and to which both sulphuric acid and alkali salts must be added. To this group belong—(*a*) clay, (*b*) cryolite, (*c*) bauxite, alumina terhydrate (Gibbsite), (*d*) refuse slack.

4. To the fourth group belong those materials, such as felspar, containing alumina and potash in sufficient quantity, but needing the addition of sulphuric acid.

Preparation of Alum from Alum-stone (*1st Group*).—Alum-stone or alunite occurs only in volcanic regions, and is the product of the action of the sulphurous vapours upon substances rich in felspar. It is found at Tolfa, near Cività Vecchia, and in large quantities at Muszag, in Hungary. The crystallised alum-stone consists of potassium and aluminium sulphates with aluminium hydroxide, according to Mitscherlich—$K_2SO_4 + Al_2(SO_4)_3 + 2(Al_2O_3 3H_2O)$.

Alum-stone loses its water at a red heat, the product of the calcination being influenced by water, while unburnt alum-stone is not. At a strong red heat the

aluminium sulphate separates into alumina, sulphurous acid, and oxygen, and the potassium sulphate is also decomposed. The mineral is calcined in lime-kilns in the ordinary manner or in reverberatories. The calcined alum-stone is lixiviated with boiling water, the supernatant liquor decanted, and the alum crystallised out. Roman, rock, or roche alum is prepared in a similar manner, the red colour being due to peroxide of iron.* Latterly, the calcined stone is lixiviated with dilute sulphuric acid instead of water.

Preparation of Alum from Alum-Shale and Alum-Earths (*2nd Group*).—This mode of preparation yields the greatest amount of alum with as much facility as does alum-stone.

Alum-Shale.—Alum-shale or schist is a sulphurous iron pyrites found under beds of clay in Upper Bavaria, in Prussia, near Düsseldorf, Saxony, Bohemia, Belgium, Hurlet and Campsie, near Glasgow, &c. Only very inferior kinds require an addition of alkali salts.

Alum-Earths.—Alum-earth is more or less a mixture of weathered iron pyrites with various bituminous matters. The sulphur is present partly in a free state, partly as iron and vitriol pyrites; the iron is present partly as sulphide, partly as iron humate.

Preparation of Alum.—The preparation of the alum may be considered in the following six operations:—

1. *Roasting the Alum-Earth.*—The roasting of the alum-earth is the easiest of the operations. The greater part of the alum manufactured is produced by precipitating aluminium sulphate with a solution of alkali salts. It is not always necessary that the schist should be burnt to concentrate the aluminium sulphate, a lengthy weathering being sufficient. The action may be explained as follows:—By the weathering, the iron bisulphide absorbs oxygen, to form iron sulphate, which separates into protoxide of iron and sulphuric acid, the latter acting upon the alumina forming an equivalent quantity of aluminium sulphate. Or by roasting, the bisulphide is decomposed to monosulphide and sulphur, which, with the sulphur of the alum-earth, gives rise to sulphurous acid, and this acting upon the alumina produces aluminium sulphate and sulphite. The roasting or calcination, however, should not take place with earths that have been subjected to less than a year's weathering, as there is found to be in practice a loss of one-sixth of the aluminium sulphate.

2. *Lixiviation.*—The lixiviation of the calcined alum earths is effected in a lixiviation cistern in which the earth is placed. These tanks stand in rows of five, the best arrangement being to build them on a slope near the calcination heaps. Each vessel has a length of 6 to 7 metres, is 5 metres broad, and about 1·3 metre in height. They are three-parts filled with the burnt earth, and completely with water; the lixivium flows from the highest tank to the lowest. If the lye is not of 1·16 sp. gr. fresh shale is added.

3. *Evaporation of the Lye.*—The concentration of the raw lye by evaporation is accomplished in leaden pans. These, however, deteriorate, crack, are easily melted,

* The composition of Roman alunite, according to C. Schwarz, is—

Silica	13·40 per cent.
Alumina	35·50 „
Potassa	12·50 „
Sulphuric acid	30·00 „
Ferric oxide	0·05 „
Water	8·50 „

The alunite is most advantageous if roasted at 500°, and extracted with sulphuric acid at from 1·297 to 1·530 sp. gr. Roman alum crystallises in cubes. If such alum is dissolved in water and the liquid is heated to 100°, basic alum is deposited and the mother liquor yields on evaporation octahedral crystals. Common alum can be converted into the cubic kind by digesting with aluminium hydroxide at 40°.

and their place is now generally supplied by cisterns of masonry. But most to be preferred is Bleibtreu's method of heating with gas, introduced in the alum works on the banks of the Rhine. The treatment of the raw lye while being concentrated depends upon its condition and upon the ferrous sulphate it contains. As ferrous sulphate is commonly present in large quantities in the raw lye or liquor, many of the German alum works are also vitriol works. When, however, the quantity of ferrous sulphate is too small to admit of being advantageously treated for the preparation of copperas, the liquor is at once evaporated until it has attained a sp. gr. of 1·40. During the ebullition basic iron sulphate is deposited, the liquor becomes of yellow-red colour, assumes a somewhat slimy condition, and has to be rendered clear before alum is obtained from it. This clearing is effected by pouring the liquor into large wooden water-tight tanks; the liquor having deposited, the suspended matter is tapped or syphoned off from the sediment, and transferred to the precipitation tanks.

4. *Alum-Flour.*—The precipitation of flour of alum is effected, in case it is desired to make potash-alum by the addition to the liquor of a potash salt, or of an ammonia salt if it is desired to make ammonia-alum. The solution of the alkaline salt is called the precipitant; by the combination of the aluminium sulphate contained in the liquor with the precipitant alum is formed, and deposited as a solid salt, care being taken to prevent the formation of large crystals by keeping the liquid stirred. By this means the alum is deposited as a crystalline powder or so-called flour of alum, which by being washed with cold water can be freed from any adhering mother liquor. The precipitation was formerly effected by the addition of wood-ash lye or lant; at the present day potassium chloride obtained either from kelp, carnallite, or beet-root molasses, and potassium sulphate derived from the decomposition of kainite, are employed for this purpose. Potassium chloride is useful only when the solution contains large quantities of ferrous sulphate, which, being converted into ferric chloride, forms potassium sulphate. Potash can only be used when the lye contains enough free sulphuric acid to combine with the salt; for otherwise a portion of the aluminium sulphate would become precipitated as insoluble alumina. The ammonia salt made use of is generally ammonium sulphate; 100 parts of aluminium sulphate require for precipitation—

Potassium chloride	43·5 parts
„ sulphate	50·9 „
Ammonium sulphate	47·8 „

The liquor covering the alum-flour is somewhat of a green colour, and contains little alum, but chiefly ferroso-ferric chloride, iron and magnesium sulphates, or magnesium chloride, dependent upon whether the precipitation was effected by sulphates or by chlorides. This liquor is used for making impure alum, ferrous sulphate, or is employed in the preparation of ammonium sulphate.

5. *Washing and Re-crystallisation.*—The floury alum is generally washed in the hydro-extractor or centrifugal machine and the liquor obtained again used for preparing alum. The washed floury alum is (6) converted into large crystals by re-crystallisation, the alum at the same time being purified. For this purpose the alum-flour is dissolved in 40 per cent. of its weight of boiling water, the operation being carried on in wooden lead-lined tanks. The hot solution is run into crystallising vessels, where the crystallisation is finished, according to the temperature of the air, in eight to ten days. From this operation hardly any mother liquor remains, the vessel being almost entirely filled with alum crystals.

Preparation of Alum from Clay (*3rd Group*).—The manufacture of alum and of aluminium sulphate from such materials as contain only alumina, to which consequently sulphuric acid and alkaline salts have to be added, has come largely into practice in

England. The materials employed are:—(*a*) clay, (*b*) cryolite, (*c*) bauxite, (*d*) blast-furnace slag.

(*a*) *Preparation of Alum from Clay.*—The clay to be employed for this purpose should be as free as possible from calcium and iron carbonates. It is first gently heated in contact with air, partly with the view of dehydration, partly for the purpose of converting any iron into oxide, and lastly to render the clay more readily soluble in acids. By dehydration the clay becomes porous and fit to take up sulphuric acid by capillarity. The gently ignited and powdered clay is gradually put into sulphuric acid of 140° Tw. (= 1·52 sp. gr.) contained in a leaden pan, and heated nearly to the boiling-point. The mass effervesces and becomes thick, and is next transferred to iron tanks, where it solidifies. It is afterwards lixiviated with water, or, better, with the liquor obtained by washing the alum-flour. The lixivium, having become clear by standing, is syphoned off from the sediment, and boiled with a sufficient quantity of potassium bisulphate or ammonium sulphate from gas liquor. The hot solution is transferred to a shallow leaden pan, and kept stirred for the purpose of converting the alum on separating into flour. The flour is washed, dried, and is then converted into large crystals as described above. The product known in the trade as alum-cake is the result of the action of sulphuric acid upon clay; it is met with in a pulverised state, is used more especially in the manufacture of inferior kinds of paper, in dyeing, and as a precipitant for sewage, and contains from 13 to 17 per cent. of alumina.

(*b*) *Preparation of Alum from Cryolite.*—Since the year 1857 alum and aluminium sulphate have been prepared, along with soda, from the mineral known as cryolite or Greenland spar, $Al_2F_6 + 6NaF_2$, and consisting in 100 parts of—

Fluorine	54·5
Aluminium	13·0
Sodium	32·5

The following are the methods employed for this purpose:—

(*a*) *Decomposition of Cryolite by Ignition with Calcium Carbonate according to Thomsen's Method.*—1 molecule of cryolite is ignited with 6 molecules of calcium carbonate, carbonic acid escapes, and soluble sodium aluminate and insoluble calcium fluoride are formed — $Al_2F_6.6NaF + 6CaCO_3 = Al_2(ONa)_6 + 6CaF_2 + 6CO_2$. From the ignited mass the sodium aluminate is obtained by lixiviation with water, and into the solution carbonic acid gas is passed. The result is the precipitation of hydrated gelatinous alumina and sodium carbonate, which remains in solution. If it be desired to obtain the alumina as an earthy compact precipitate, sodium bicarbonate is used as a precipitant instead of carbonic acid. While the clear liquor is boiled down for the purpose of obtaining sodium carbonate, the precipitated alumina is dissolved in dilute sulphuric acid; this solution is evaporated for the purpose of obtaining aluminium sulphate (so-called concentrated alum), or the solution, after having been treated with a potassa or ammonia salt, is converted into alum. 100 lbs. of cryolite yield 33 lbs. of alumina, which require 90 lbs. of sulphuric acid to yield a neutral solution; 100 lbs. of cryolite will therefore yield 305 lbs. of alum, and may give in addition—

Calcined soda	75·0 lbs., or
Crystallised sodium carbonate	203·0 „ or
Caustic soda	44·0 „ or
Sodium bicarbonate	119·5 „

(*β*) *Decomposition of Cryolite with Caustic Lime by the Wet Way* (*Sauerwein's Method*).—Very finely ground cryolite is boiled with water and lime, the purer the better, and as free from iron as possible, in a leaden pan. The result is the formation of a solution of sodium aluminate and insoluble calcium fluoride—

$$Al_2Fl_6.6NaFl + 6CaO = Al_2(ONa)_6 + 6CaFl_2.$$

When the calcium fluoride has been deposited, the clear liquid is decanted, and the sediment washed, the first wash-water being added to the decanted liquor, and the second and third wash-waters being used instead of pure water at a subsequent operation. In order to separate the alumina from the solution of sodium aluminate, there is added to the liquid, while being continuously stirred, very finely pulverised cryolite in excess, the result of the decomposition being exhibited by the following formula—$Al_2(ONa)_6 + Al_2Na_6F_{12} = 2Al_2O_3 + 12NaF$. When no more caustic soda can be detected in the liquid—a small quantity of which should, after filtration, yield, upon the addition of a solution of sal-ammoniac and application of heat, a precipitate of alumina—it is left to stand for the purpose of becoming clear. The clarified solution of sodium fluoride is then drawn off, and the alumina treated as above described. The solution of sodium fluoride having been boiled with caustic lime yields a caustic soda solution which, having been decanted from the sediment of calcium fluoride, is evaporated to dryness. The calcium fluoride obtained as a bye-product of the cryolite industry is now used in glass-making.

(γ) The decomposition of cryolite by sulphuric acid yields sodium sulphate, convertible into carbonate by Leblanc's process, and aluminium sulphate free from iron. 238 parts of cryolite require for decomposition 240 parts of anhydrous or 321 parts of ordinary sulphuric acid. The resulting compounds are aluminium sulphate, sodium sulphate, and hydrofluoric acid: $Al_2Na_6F_{12} + 6H_2SO_4 = Al_2(SO_4)_3 3Na_2SO_4 + 12HF$. This method of decomposing cryolite is, however, by no means to be recommended, as, owing to the liberation of hydrofluoric acid, peculiarly constructed apparatus are required; while the sodium sulphate has to be converted into sodium carbonate. Persoz suggests that cryolite should be treated in platinum vessels with three times its weight of strong sulphuric acid, to be recovered with the hydrofluoric acid by distillation. The solid residue should be treated with cold water in order to dissolve the larger part of the sodium bisulphate contained in the saline mass, from which the anhydrous aluminium sulphate is extracted with boiling water, and converted by the addition of potassium or ammonium sulphate into alum free from iron. The solution of sodium bisulphate, having been evaporated to dryness, is employed for the preparation of fuming sulphuric acid, Glauber's salt remaining as a residue.

(*c*) *Preparation of Alum from Bauxite.*—In some parts of Southern France, in Calabria, near Belfast, Ireland, and other parts of Europe, a mineral occurs consisting essentially (60 per cent.) of hydrated alumina of greater or less purity, termed bauxite, from the fact of having been first found in the commune of Baux, in France. In order to prepare alum and aluminium sulphate from this mineral, it is first disintegrated by being ignited with sodium carbonate, or with a mixture of sodium sulphate and charcoal; in each instance the lixiviation of the ignited mass yields sodium aluminate, from which, by processes already described under Cryolite, alum, or aluminium sulphate and soda are prepared.

(*d*) *Preparation of Alum from Blast-Furnace Slag.*—J. Lürmann recommends that the slag should be decomposed by means of hydrochloric acid. From the resulting solution of aluminium chloride * the alumina is precipitated by calcium carbonate, any dissolved silica being precipitated at the same time. The alumina is dissolved in sulphuric acid, leaving the silica; 100 kilos. of slag containing 25 per cent. of alumina yield 180 kilos. of alum and 31 kilos. of silica.

Alum from Felspar (*4th Group*).—The manufacture of alum from minerals (for instance, felspar) containing alumina and potassa is not of any industrial importance.

* Crude aluminium chloride is used as a disinfectant under the name of chloralum, and as a precipitant for sewage. Compare Slater's *Sewage Treatment.*

Properties of Alum.—Potash-alum, $\left.\begin{matrix}Al_2\\K_2\end{matrix}\right\}4SO_4 + 24H_2O$, or $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O$, consists in 100 parts of—

Potassa	9·95
Alumina	10·83
Sulphuric acid	33·71
Water	45·51*
	100·00

It crystallises readily in regular octahedra, loses at 60° 18 mols. of water, and fuses at 92° in its water of crystallisation, yielding a colourless fluid which retains its state of aggregation for some time after cooling before it solidifies into a crystalline mass. At a temperature a little below red heat alum loses all its water, becoming converted into burnt-alum, *alumen ustum*, a white, porous, readily friable mass. When ignited with carbonaceous matter, air being excluded, potash-alum forms a pyrophoric compound.

100 parts of water at		0°	dissolve	3·9	parts of	potash-alum
,,	,,	20	,,	15·8	,,	,,
,,	,,	40	,,	31·2	,,	,,
,,	,,	100	,,	360·0	,,	,,

The solution of alum in water (the salt is insoluble in alcohol) has an astringent, sweet taste, and possesses an acid reaction so strong that when alum is heated with common salt hydrochloric acid is evolved; while a concentrated solution of alum destroys the blue colour of many—not of all—artificial ultramarines.

Ammonia Alum.—This salt,

$$\left.\begin{matrix}Al_2\\(NH_4)_2\end{matrix}\right\}4SO_4 + 24H_2O, \text{ or } (NH_4)_2SO_4 + Al_2(SO_4)_3 + 24H_2O,$$

consists in 100 parts of:

Ammonia	3·89
Alumina	11·90
Sulphuric acid	35·10
Water	48·11
	100·00

Ammonia-alum is now far more extensively manufactured than potash-alum. When ammonia-alum is strongly heated, ammonium sulphate, water, and sulphuric acid are driven off, and alumina remains.

100 parts of water at		0°	dissolve	5·22	parts of	ammonia-alum
,,	,,	20	,,	13·05	,,	,,
,,	,,	40	,,	27·27	,,	,,
,,	,,	100	,,	421·90	,,	,,

Soda-Alum.—The formula of this salt is—

$$\left.\begin{matrix}Al_2\\Na_2\end{matrix}\right\}4SO_4 + 24H_2O, \text{ or } Na_2SO_4 + Al_2(SO_4)_3 + 24H_2O,$$

containing in 100 parts—

Soda	6·8
Alumina	11·2
Sulphuric acid	34·9
Water	47·1
	100·0

It is as readily prepared from aluminium sulphate and sodium sulphate as the alums already mentioned, but its solubility prevents the separation from the mother

* Maumene questions the existence of 45·51 per cent. of water in alum.

liquor, while its solution when boiled loses the property of crystallising. As iron cannot be removed from this salt by re-crystallisation, the materials it is obtained from should be free from that metal. The solutions should be mixed cold, and gently evaporated at a temperature not exceeding 60°.

Neutral or cubical alum ($K_2SO_4 + Al_2O_3,2SO_3$) is obtained either by adding to an alum solution so much potassium or sodium carbonate as will begin to separate the alumina, or a solution of alum is treated with gelatinous alumina. By boiling 12 parts of alum and 1 part of slaked lime in water, the same salt is obtained. This neutral salt is often preferred in dyeing and calico printing, as it does not affect certain colours. When ammonia-alum is similarly treated, it also yields a neutral alum. Blesser (*a*) and Schmidt (*b*) found the following to be the composition of cubical alum in 100 parts:—

	(*a*)		(*b*)
Sulphuric acid	34·52	...	33·95
Alumina	11·86	...	11·48
Potassa	9·44	...	9·04
Water	45·27	...	45·61
	101·09	...	100·08

Insoluble or basic alum, $Al_2K_2.2SO_4$, is obtained by boiling a solution of alum with hydrate of alumina; it is a white, insoluble powder, and as regards its composition similar to alum-stone. Basic alum is soluble in acetic acid.

Aluminium Sulphate.—The active principle of alum is evidently the aluminium sulphate, not the potassium and ammonium sulphates, the object of the preparation of the double salt being simply the obtaining of a definite compound, which, while it readily crystallises, can be obtained in a pure state, especially free from iron, a very injurious ingredient in alum used in dyeing and calico-printing.* However, at the present day, with improved methods of manufacture, aluminium sulphate is largely prepared, and of excellent quality. It is often sold under the name of concentrated alum or cake alum, as it occurs in the trade as square cakes. It is white, somewhat transparent, and may be cut with a knife; is readily soluble in water, contains always free sulphuric acid, and also to some extent potassa- and soda-alum.

In the pure state this salt has the formula $Al_2(SO_4)_3 + 18H_2O$, and contains in 100 parts—alumina, 18·78; sulphuric acid, 38·27; water, 42·95; total, 100. That the composition of this salt as met with in commerce varies greatly may be inferred from the following results of Varrentrapp's analyses of different samples of this salt:—

	1.		2.		3.		4.
Alumina . . .	15·3	...	12·5	...	15·1	...	13·0
Sulphuric acid . .	38·0	...	30·6	...	38·0	...	34·0

According to the formula, the quantity of sulphuric acid in these samples should have been—

1.		2.		3.		4.
35·8	...	29·2	...	43·3	...	30·5

The quantity of water even varies between 56 and 48 per cent. for different parts of the same cake. Weygand found a sample of this salt prepared at Schwemsal to contain—alumina, 15·57; sulphuric acid, 38·13; oxide of iron, 1·15; potassa, 0·62; water, 45·79 parts. The aluminium sulphate prepared from cryolite at Harburg contains about 5 per cent. of sodium sulphate. The results obtained in the analyses by H. Fleck of various samples of cake-alum are—

* An almost infinitesimal trace of iron renders alum unfit for dyeing alazarine reds or roses.

Aluminium sulphate . . .	47·35 ...	50·80 ...	51·63
Sodium „ . . .	4·35 ...	1·24 ...	0·77
Free sulphuric acid . . .	0·73 ...	0·27 ...	—
Water	47·37 ...	47·47 ...	46·94
	99·80 ...	99·78 ...	99·34

Cake-alum is prepared either from clay, cryolite, or bauxite, by methods already described. When clay is employed, the iron has to be removed from the dilute solution of the aluminium sulphate by precipitation as Berlin blue by means of potassium ferrocyanide. When cryolite is used, the alumina, separated from the solution of sodium aluminate by carbonic acid or powdered cryolite, is put into sulphuric acid, contained in a wooden lead-lined tank, and heated to 80° to 90°, the addition of the alumina to the acid being continued until solution ceases to take place. The solution having been clarified by standing for some time is next evaporated in a copper vessel until the salt fuses; it is then cast into moulds. With due care aluminium sulphate may be used in dyeing and calico-printing, but it cannot be altogether substituted for alum, owing to its variable composition.

Aluminium hydrochlorate, formerly known as muriate of alumina, may be prepared in an impure state by the process of Georges Fournier, who lixiviates pyritic alum shales, previously well weathered, allows ferrous sulphate to crystallise out and adds to the residual lye of aluminium sulphate containing iron sulphate, sodium chloride. At temperatures of – 1° or – 2° sodium sulphate crystallises out and is drained by whizzing. The mother liquor is aluminium hydrochlorate.

Slater dissolves in crude hydrochloric acid a mineral found in the North of Ireland which differs from bauxite by containing 3 instead of 2 mols. of combined water and by being easily soluble in hydrochloric acid. Both these forms of aluminium hydrochlorate are well adapted for the treatment of sewage and refuse waters by precipitation.

Sodium Aluminate.—Sodium aluminate is now prepared on the large scale, as it has been found to be a useful form of soluble alumina, especially in dyeing and calico-printing. The preparation of this compound is based upon the solubility of aluminium hydroxide in caustic potassa- or soda-lye, and the ready decomposition of the solution by carbonic and acetic acids, sodium bicarbonate and sodium acetate, sal-ammoniac, &c.

Sodium aluminate was first brought under the notice of dyers by Macquer and Hausmann in 1819, but owing to the preparation being too expensive it did not come into industrial application until comparatively recently. We have already described the mode of manufacturing sodium aluminate from cryolite; but in Germany—the chief seat of the cryolite industry—this salt is not made on the large scale; in France it is manufactured by Merle & Co., at Alais, and in England at the Washington Chemical Works. In France bauxite, containing 60 to 75 per cent. of alumina and from 12 to 20 per cent. of oxide of iron, is the raw material, and is treated with sodium hydroxide or carbonate. If caustic soda is used, the pulverised mineral is boiled with a solution of the alkali; while if the carbonate is employed, the mixture is ignited in a reverberatory furnace. In either case sodium aluminate is produced, dissolved—in the case of ignition, the semi-fused mass is lixiviated with water—and evaporated to dryness. The salt met with in commerce is a white powder with a green-yellow hue, dry to the touch, and consisting of—

Alumina	48
Soda	44
Sodium chloride and sulphate . . .	8
	100

The formula, $\left.\begin{matrix}Al_2\\Na_6\end{matrix}\right\}O_6$, would require —

Alumina	52·79
Soda	47·21
	100·00

Sodium aluminate is equally soluble in cold and hot water. Exposed to air it absorbs moisture and carbonic acid, and consequently on being dissolved in water the salt so changed yields a turbid solution, owing to alumina being suspended. The aqueous solution of this salt is not stronger than 14° to 18° Tw. = 1·07 to 1·09 sp. gr. According to Le Chatelier, Deville, and Jacquemart, aluminium sulphate is the starting-point of the preparation of sodium aluminate by precipitating from the sulphate the alumina, and re-dissolving the latter in caustic soda-lye. Sodium aluminate is largely used in the preparation of an opaque, milky-looking glass, or semi-porcelain. Sodium aluminate is a bye-product of Balara's method of soda manufacture from bauxite, Glauber's salt, and coal; this bye-product, or rather product of the second stage of the process, is decomposed by carbonic acid into sodium carbonate and alumina, which is thrown down. The Pennsylvania Salt Manufacturing Company at Natrona, near Pittsburg, manufacture large quantities of sodium aluminate, which is used in soap-boiling under the name of *natrona refined saponifier*.*

Aluminium Hydrate, $Al_2(OH)_6$, is obtained by adding to sodium aluminate cream of lime, when insoluble calcium aluminate separates out—

$$Al_2(ONa)_6 + 3Ca(OH)_2 = 6Na(OH) + Ca_3Al_2O_6.$$

After washing, the precipitate is dissolved in hydrochloric acid, and the solution decomposed with a fresh quantity of calcium aluminate, when aluminium hydroxide is deposited, which is washed and dried—

$$Ca_3Al_2O_6 + 12HCl = 3CaCl_2 + Al_2Cl_6 + 6H_2O.$$
$$Al_2Cl_6 + Ca_3Al_2O_6 + 6H_2O = 3CaCl_2 + 2Al_2(OH)_6.$$

Aluminium hydrate is obtained also on precipitating a solution of sodium with carbonic acid, sodium bicarbonate, or sal-ammoniac, or by precipitating a solution of alum with sodium carbonate.

Aluminium hypochlorite has been proposed for bleaching; aluminium sulphite for disinfection and for preserving articles of animal food; and aluminium oxalate for preserving articles of marble, dolomite, &c. Aluminium chloride, free from iron, &c., was proposed some time ago as a disinfectant, under the name of chloralum, but at present it is used for "carbonising" wool. Aluminium acetate is used in dyeing† (*see* Mordants).

A very questionable aluminium carbonate has been proposed for sanitary purposes.

Applications of Alum and Aluminium Salts.—Owing to the great affinity of the alumina contained in alum for textile fibres, especially wool and cotton, alum is largely used as a mordant in dyeing, except when the tar colours are employed. Again, owing to the affinity of alumina for many pigments, alum is employed in the preparation of the lake colours, combinations of active colouring principles with alumina. It is also used in the melting of tallow; for hardening gypsum; it is found in the preparation used for sizing hand-made paper, the alum in this case forming with the glue or size an insoluble compound. Alum with resin is employed for the same purpose in machine-made paper, an aluminium pinate being formed. It is very largely used for the preparation of aluminium acetate, and with common salt in the tawing of leather. Alum is employed in clarifying turbid fluids, more especially water; in this case the

* Sodium aluminate is used by Maxwell Lyte for the treatment of soda by precipitation, for which purpose it is very suitable.

† Aluminium acetate, for the production of alizarine roses and reds in dyeing and tissue-printing, is being to some extent superseded by aluminium sulphocyanide (rhodanide). Compare Hummel, *Dyeing of Textile Fabrics*, p. 172. Aluminium nitrate is also occasionally used as a mordant.

alum takes up the alumina suspended in the water, and, forming an insoluble (basic) alum, carries down organic and other suspended impurities. A boiling solution of alum, common salt, and potassium nitrate is used by jewellers for the purpose of colouring gold—that is to say, to produce a film of pure gold on the alloy, the copper of which is dissolved by the boiling solution. Sodium aluminate is used in dyeing and calico-printing; further, for the preparation of lake colours, the induration of stone, and the manufacture of artificial stone, and for the saponification of fats in the stearine candle manufacture, an alumina soap being first formed, which is decomposed by acetic acid into aluminium acetate and free fatty acid.

ULTRAMARINE.

Ultramarine is a splendid blue colour, formerly obtained in small quantities from lazulite. Its analysis led to the production of artificial ultramarine—an invention ascribed by the French to Guimet, but by the Germans to C. Gmelin.

Raw Materials.—These are—1. Aluminium silicate as free as possible from iron, a good china clay, the kaolin of Cornwall being esteemed the best; 2. Calcined sodium sulphate; 3. Calcined soda; 4. Sodium sulphide, as a bye-product of the manufacture; 5. Sulphur; 6. Pulverised charcoal, or pit-coal.

Porcelain, or china clay, is generally used, or a white clay, the composition of which is nearly the same. Small quantities of lime and magnesia have no injurious effect, but the oxide of iron should not exceed 1 per cent. The composition of the clay should approach as nearly as possible to the formula $H_2Al_2Si_2O_8$; the silica may be combined or partly free. The clay is washed with water and treated in the same manner as for making porcelain; it is next dried, ignited, and ground to a very fine powder. The sodium sulphate should not contain any free acid, lead, or iron. If the sulphate does not possess the requisite qualities, it is dissolved in water, milk of lime being added to neutralise the acid and to precipitate oxide of iron. The clear solution is left to crystallise, and the crystals are ignited in a reverberatory furnace and then pulverised. The clear solution is in some cases evaporated to dryness and ignited in iron vessels. Barium, but not potassium, salts form ultramarine.* The calcined soda is obtained from the alkali works, and should contain at least 90 per cent. of sodium carbonate; it is also finely pulverised. Very recently caustic soda has been substituted in some ultramarine works. Sodium sulphide (Na_2S) is usually a bye-product of the process of making ultramarine, and is obtained either in solution or as a dry powder. The sulphur is used very finely pulverised. The carbonaceous matter employed is also in a very fine powder. Its use was introduced by Leykauf for the purpose of deoxidation. In order to have the carbon in as finely divided a state as possible it is ground to a pulp with water under granite stones; the pulp is lixiviated, and the fine powder obtained dried and passed through a sieve; in some cases resin and pitch are employed. For ultramarines which must not have their colour discharged by alum, pure silica, either as fine glass, sand, or pulverised quartz, is used. Several substances are used to reduce the depth of colour of ultramarine—viz., gypsum, barium, sulphate, baryta white, and flour; the last is employed in making up washing blue.

Manufacture of Ultramarine.—The methods of ultramarine preparation may be classified, according to the crude materials employed, as the three following:—

(*a*) Preparation of sulphate, or Glauber's salt, ultramarine.
(*b*) „ „ soda-ultramarine.
(*c*) „ „ silica-ultramarine.

(*a*) *Preparation of Sulphate-Ultramarine.*—This ultramarine is prepared according

* See *Chemical News*, vol. xxiii. pp. 119, 142, 204.

to the Nuremberg process from kaolin, sodium sulphate, and charcoal; the preparation consisting in two distinct stages, viz.:—

(*a*) Preparation of green ultramarine.

(*β*) Conversion of green into blue ultramarine.

(*a*) *Preparation of Green Ultramarine.*—In order to obtain a most intimate mixture of the dry and finely pulverised materials, small quantities are weighed off, mixed in wooden troughs by means of shovels, and several times passed through sieves. If solutions of Glauber's salt, soda, and sodium sulphide are used instead of powders the kaolin is mixed with these solutions, and the whole evaporated to dryness, gently ignited in a reverberatory furnace, and then pulverised and sifted. The quantities of the crude materials vary, but the following conditions have to be complied with:— 1. Soda, whether sulphate or caustic, must be present in such quantity that it can saturate half of the silica of the clay (kaolin). 2. There must be sufficient soda remaining to form with the sulphur a certain quantity of sodium polysulphide. 3. There ought to remain enough sulphur and sodium to form another sodium sulphide (Na_2S) after deducting from the whole mixture as much green ultramarine as, according to its composition as proved by recent analysis, the silica and alumina present are capable of forming. The following figures will give an idea of the proportions:—

	I.		II.
Kaolin (dried)	100	...	100
Calcined Glauber's salt	83–100	...	41
Calcined soda	—	...	41
Carbon (char- or pit-coal)	17	...	17
Sulphur	—	...	13

For 100 parts of calcined soda 80 parts of calcined Glauber's salt, and for 100 parts of the latter 60 of dry sodium sulphide, are taken.

It is usual to have a large quantity of this mixture prepared for use. If this mixture is ignited without access of air, a white mass is obtained, which, having been treated with water, is a light, somewhat flocculent, white substance, to which Ritter has given the name of white ultramarine. It becomes green by exposure to air, and blue by being calcined in contact with air. The mixture is well rammed into fire-clay crucibles, placed in furnaces similar in construction to those used for burning porcelain, being raised to, and maintained at, a high temperature with a very limited supply of air. This operation lasts from seven to ten hours, and is completed at a bright white heat. The furnace is closed and slowly cooled; on removing the crucibles, the contents appear as a semi-fused grey- or yellow-green mass, which is repeatedly treated with water. The ultramarine thus obtained is in porous lumps, which are pulverised into an impalpable powder; this is washed, dried, and again ground, then sifted, and finally packed in boxes or casks, and sent into the market as green ultramarine, consisting, according to Stölzel's analysis (1855), in 100 parts, of—

Alumina	30·11	
Iron	0·49	(ferric oxide, 0·7)
Calcium	0·45	
Sodium	19·09	(soda, 25·73)
Silica	37·46	
Sulphuric acid	0·76	
Sulphur	6·08	
Chlorine	0·37	
Magnesia, potassa, phosphoric acid	traces	
	94·81	
Oxygen	5·19	
	100·00	

Green ultramarine is a pigment of comparatively inferior value, owing to its being less brilliant than the green copper pigments.

(β) *Conversion of Green into Blue Ultramarine.*—This operation may be variously effected, generally by roasting the green ultramarine and sulphur at a low temperature with access of air, so as to form sulphurous acid, while a portion of the sodium is oxidised into soluble sulphate and afterwards washed out; but the sulphur originally present in the green ultramarine remains combined with a smaller quantity of sodium. The roasting may be variously carried out, but very frequently the apparatus consists of a fixed iron cylinder similar to a gas-retort, provided with a stirring apparatus, by means of which the mixture of green ultramarine and sulphur (25 to 30 lbs. of the former to 1 lb. of sulphur) is submitted equally to the source of heat. The addition of sulphur is repeated until the desired blue colour is produced; but in some works this calcination is interrupted by repeated lixiviation, the object being to produce a superior article. Muffle-ovens and a kind of reverberatory oven are also used for this operation. The sulphurous acid, which is evolved in large quantities, is now generally employed in making sulphuric acid, sometimes a co-product of ultramarine manufacture, and used for the preparation of the sodium sulphate required. The ultramarine, when quite blue, is pulverised, lixiviated, dried, and finally separated into various qualities known in the trade as No. 00, 1, 2, 3, &c.

(*b*) *Preparation of Soda-Ultramarine.*—As manufactured in France, Belgium, and some parts of Germany, this ultramarine is either pure soda-ultramarine or a mixture of soda- and sulphate-ultramarine. The materials and proportions are—

	I.	II.	III.
Kaolin	100	100	100
Sulphate	—	41	—
Soda	100	41	90
Carbon (char- or pit-coal)	12	17	6
Sulphur	60	13	100
Rosin	—	—	6

The ignition takes place either in crucibles, or, better, in a reverberatory furnace; the result is the formation of a brittle and porous green substance, which absorbs oxygen very rapidly, so that, during the cooling of the mass in the oven, the greater part is converted into blue ultramarine.* The complete conversion, after the addition of sulphur, is obtained by heating to redness in large muffles, the bottoms of which consist of plates of fire-clay and the lids of iron, the product being distinguished from the foregoing by a greater depth and beauty of colour. By increasing, within certain limits, the quantities of soda and sulphur, the formation of blue ultramarine may be at once obtained, the product containing 10 to 12 per cent. of sulphur.

(*c*) *Preparation of Silica-Ultramarine.*—Silica-ultramarine is really soda-ultramarine in the preparation of which silica to the amount of 5 to 10 per cent. of the weight of the kaolin is added. The calcination at once yields blue ultramarine, and further treatment with sulphur is therefore unnecessary.

This ultramarine is not acted upon by a solution of alum, and may be recognised by its peculiar red hue, the intensity of which is increased by an increase of silica. Notwithstanding the superiority of the ultramarine obtained by this process, its preparation is disadvantageous owing to the tendency of the mixture of crude materials to fuse during ignition.

The composition of the two chief kinds of ultramarine with a reddish blue (I.) and a pure blue tone (II.) appears from the following analysis by R. Hofmann :—

* Ultramarine green cannot be obtained by this process.

	I.		II.
Clay residues	3·61	...	2·11
Silica	40·77	...	37·77
Alumina	23·74	...	29·54
Potassa	0·83	...	1·38
Soda	18·54	...	21·61
Sulphur	13·58	...	7·87
	101·07	...	100.28

Siliceous blues from the Hirschberg works (I. to IV.) and from the Marienberg works (V. and VI.) had, according to Guckelberger's analysis, the following compositions:—

	I.	II.	III.	IV.	V.	VI.
Si	19·2	19·0	19·0	19·3	19·3	19·0
Al	12·6	12·7	13·0	12·5	12·8	13·0
Na	16·5	16·8	16·5	16·8	16·1	15·9
S	14·2	14·0	13·8	13·9	14·0	14·0
O	37·5	37·5	37·7	37·5	37·8	38·1

Since 1873 the Nüremberg Ultramarine Works produces *violet* and *red* ultramarine. These kinds are obtained by treating blue, green, or white ultramarine, at a high temperature and with access of air, with acids or salts which give off acids if strongly heated. A violet is first formed, and on heating more strongly a red. Violet ultramarine can also be obtained by hydroxylating the blue and the green kinds.

Constitution of Ultramarine.—The cause of the blue colour of ultramarine has been the subject of repeated investigation. In 1758, Marggraf refuted the view then prevalent that lazulite contained copper, which was the cause of its colour. As he detected the presence of iron he thought this metal must be the colouring principle. Guyton de Morveau ascribed the colour to iron sulphide.

As according to Guckelberger there are in the colour almost exactly Na_2CaSi_2, the charge must contain Si_2Na_4. On exposure to the action of SO_2 at a suitable temperature, without escape of oxygen, there is formed from $Na_2 + 2SO_2 = S + Na_2SO_4$—*i.e.*, the nascent sulphur fills up the vacancy formed by the exit of Na_2; we may, therefore, obtain from $Si_2Al_2Na_4O_9$, the compound $Si_2Al_2Na_2SO_9$—*i.e.*, ultramarine blue. Hence there is no Na_2S in the compound, and if on the action of aqueous acids H_2S, or along with it SO_2, is obtained and free sulphur is separated out, this ensues because the constituents of water combine with the nascent sulphur. The composition of ultramarine green agrees with the formula $Si_6Al_6Na_8S_2O_{24}$. Under the influence of heat the 5 mols. Na_2SO_4 of the charge are converted by carbon into $5Na_2SO_3$. With the increase of temperature 4 mols. Na_2SO_3 are resolved into $3Na_2SO_4 + Na_2S$. The fifth mol. may for the first be considered as unaltered. The regenerated sulphate (3 mols.) is again reduced by carbon to $3Na_2SO_3$, which along with the still existing mol. Na_2SO_3 undergo the well-known change on heating, so that in a certain stage there are present $3Na_2SO_4$ and $2Na_2S$. On increase of temperature the SiO_2 enters into reaction, and by the aid of carbon it withdraws Na_2O from sodium sulphate. There is formed $Si_6Al_6Na_6O_{24}$, an unsaturated nucleus with two free affinities. The escaping SO_2 acts upon the existing $2Na_2S$; there are formed sulphate and 2NaS, which satisfy the free affinities of the nucleus.

In the blue strata the same process goes on at first, but the SO_2 escaping from the green acts by removing sodium, so that $\frac{3}{5}$ sulphur must be found in the crude green and $\frac{1}{5}$ in the crude sulphur, as experiment has shown $\frac{4}{5}$ sulphur escapes partly as SO_2 and partly free. The compound examined by Silber is, according to Guckelberger, to be considered as $Si_6Al_6Na_4(OH)_2O_{23}$. If we suppose in this compound HO replaced by the equivalent NaS, the simplest expression for ultramarine blue will be =

$Si_6Al_6Na_4(NaS)_2O_{23}$. The siliceous colour, $Si_6Al_6Na_4(NaS)_2 + S_2$, contains the sulphur, either as NaS—S, or we have —S—S—, instead of Al_2O_3.

Properties of Ultramarine.—Artificial ultramarine is an impalpable powder of a fine blue colour, entirely insoluble in water, and, when washed with distilled water, leaving no residue on evaporation of the filtrate. It is not acted upon by alkalies, but is highly sensitive to the action of even very dilute acids and acid salts, sulphuretted hydrogen being evolved and the colour discharged. Native ultramarine obtained from *lapis lazuli* is not thus decomposed by weak acid solution. There sometimes accidentally occurs in soda furnaces a more or less blue ultramarine which exhibits the same resistance to acids. That kind of ultramarine commercially termed acid proof is manufactured with the addition of silica, as described, but it really only resists the action of alum-salts. Ultramarine is now largely used for the purposes to which smalt, litmus, and Berlin blue were applied—that is to say, ultramarine is employed as a paint, as a pigment in stereochromy, for paper-hangings, calico-printing with albumen as fixing material, for colouring printing-ink, for the bluing of linen and cotton fabrics, paper, stearine- and paraffine-candles, and lump-sugar. For 1000 cwts. of sugar $2\frac{1}{2}$ lbs. of the pigment are employed, a quantity so small as to be perfectly innocuous; further, ultramarine does not contain anything injurious to health. Green ultramarine is a dull-coloured powder used by wall-paper stainers, and is sometimes mixed with indigo-carmine and a yellow pigment to improve the colour.

Adulterations of ultramarine with Berlin blue, smalt, and other blue pigments do not now occur, as ultramarine is a cheaper material; but to obtain lighter tints, ultramarine is sometimes mixed with chalk, kaolin, alabaster, and chiefly with barium sulphate.

COMPOUNDS OF TIN AND ANTIMONY.

Mosaic Gold (*Aurum Musivum*).—The substance known under this name is in reality a bisulphide of tin (SnS_2), prepared in the following manner:—4 parts of pure tin, with 2 of mercury, are amalgamated by the aid of a gentle heat, and introduced with $2\frac{1}{2}$ parts of sulphur and 2 of sal-ammoniac into a flask, and heated on a sand-bath, at first gently, and then gradually increasing to a full red heat. First the sal-ammoniac volatilises, and next mercury in the shape of cinnabar mixed with a trace of the sulphide of tin; while there is left the preparation known as mosaic gold, forming the upper layer of the remaining contents of the flask, the lower portion being of badly coloured sulphide. The *rationale* of the formation of this peculiar coloured sulphide—that is, peculiar as regards its physical appearance—is not quite clearly explained; the compound, moreover, may be prepared without mercury. When properly prepared, it appears as a golden-coloured metallic substance, greasy to the touch, and soluble in the alkaline sulphurets. It is chiefly used for imitating gilding on painted surfaces, but its employment is very much restricted from the fact that the bronze-colours give a more satisfactory result. Indeed, in the English market mosaic gold is almost obsolete.

Tin Crystals (solid) (*Stannous Chloride*, $SnCl_2.2H_2O$).—By the name of tin-salt the trade understands chloride of tin ($SnCl_2$), but the commercial article, being prepared by dissolving granulated tin in hydrochloric acid and evaporating the solution, is really $SnCl_2 + 2H_2O$. According to H. Nöllner, hydrochloric acid gas should be caused to act on granulated tin placed in earthenware receivers, and the concentrated tin-salt solution thus obtained evaporated in block-tin vessels. The salt occurs in the trade in colourless, transparent, diliquescent crystals, of course very soluble in water. The aqueous solution, unless acidulated with more hydrochloric or tartaric acid, soon deposits a basic salt. Tin-salt is used chiefly in dyeing and calico-printing.*

* Copper vessels may be used for dissolving tin in hydrochloric acid, as whilst any tin remains undissolved the copper is not attacked. Stannous chloride is also used in the liquid state as single

Tin Chloride, Stannic Chloride ($SnCl_4 5H_2O$) is obtained by dissolving stannic oxide in hydrochloric acid. If it be desired to obtain the solid stannic chloride, the solution is mixed with clean sand or infusorial earth, dried and distilled in a current of superheated steam.*

The so-called "nitrate of tin" is made by dissolving grain bar tin (not granulated) in single aquafortis, which must be absolutely free from sulphuric acid or the lower oxides of nitrogen, though it may contain a proportion of hydrochloric acid. The operation must be conducted very carefully, the temperature must not be allowed to rise, and no red fumes must be given off. This mordant, which is of a peculiar reddish yellow colour, served in grounding cochineal scarlets, is now consequently nearly fallen into disuse.

Pink Salt, $SnCl_4 + 2NH_4Cl$, is used in tissue-printing, though less in Britain than on the Continent. A concentrated solution of this salt is not affected by boiling, but if diluted it deposits all its stannic oxide upon the fibre. Its neutral character is its great recommendation.

Stannate of Soda, *preparing salt* (Na_2SnO_3).—This salt is now very largely used in dyeing as well as in calico-printing, and is prepared in various ways, sometimes by fusing tin-ores with caustic soda and lixiviating the molten mass with water; or, according to Brown, by boiling soda lye with metallic tin and litharge, the effect being the formation of sodium stannate and metallic lead. Häffely somewhat modifies this process by digesting litharge with soda lye at 22 per cent. in a metallic vessel. Into the solution of sodium plumbate thus obtained, granulated tin is placed and heat applied. Sometimes a sodium stannite is used, made by dissolving tin-salt in an excess of caustic soda, but this preparation is unstable and does not answer well in dyeing and printing; it is only extemporaneously used on a limited scale by small dyers.†

COMPOUNDS OF ANTIMONY.

Antimony Oxide.—This substance (Sb_2O_3), obtained by calcining antimony sulphide, or by the precipitation of a solution of antimony chloride with a solution of sodium carbonate, finally washing and drying the precipitate, has of late been used as a substitute for white-lead, but it does not cover so well and is more expensive, though it is not affected by sulphuretted hydrogen. As this oxide takes up oxygen in the presence of alkalies, and is converted into antimonic acid (Sb_2O_5), it has been lately proposed for use in the preparation of aniline red and for the conversion of nitrobenzol into aniline; also for the preparation of calcium iodide by keeping antimonic oxide suspended in milk of lime, and adding iodine as long as the latter is taken up.

Black Antimony Sulphide.—This compound (Sb_2S_3), obtained by liquation, occurs in commerce in the conical shape it has assumed while cooling; its colour is like that of graphite, but it has a stronger metallic lustre, is of a deeper black colour, a fibrous, crystalline structure, and very brittle; it usually contains iron, lead, copper, and arsenic, and is employed for separating gold from silver, in veterinary surgery, pyrotechny, and in

and double muriates, differing merely in their concentration; single muriates vary from 40° to 60° Tw. and double muriates from 70° to 120°. The former contain 1 to 2 oz. metallic tin in the pound, and the double kind from 2½ to 5 oz. All forms of stannous chloride are used as mordants. See Slater: *Manual of Colours and Dye Wares.*

* The various liquids used by dyers and printers under the names of solution, composition, &c., are made by dissolving metallic tin in mixtures of hydrochloric acid and nitric acid, differing greatly in strength and proportions, and with or without the addition of alkaline chlorides. Oxalic acid or tartaric acid is often added to the finished solution.

† The author states that "some years ago the use of a double sodium salt of arsenic and stannic acids was introduced among English dyers." The use of this dangerous preparation, though not prohibited by law, is condemned by the best authorities as affording no advantages commensurate with its poisonous properties.

the preparation of the percussion pellets used in the cartridges of the now celebrated Prussian needle-gun.

Neapolitan Yellow.—This pigment, used as an oil paint and in glass and porcelain staining, is of an orange-yellow colour, and very permanent. It is lead antimoniate, and is prepared as follows:—1 part of potassium antimonio-tartrate (tartar emetic), 2 parts of lead nitrate, and 4 parts of common salt, are fused at a moderate red heat, and kept at that temperature for two hours. The molten mass is put after cooling into water and becomes disintegrated, the salt dissolving and the pigment precipitating. When required for staining glass or porcelain it is mixed with a lead-glass. It has recently been prepared by roasting a mixture of antimonious acid and litharge.

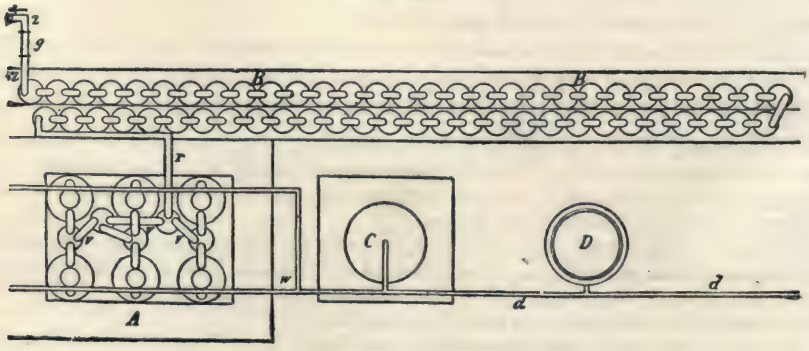
Antimony Cinnabar.—Antimony oxysulphide ($Sb_6S_6O_3$), is a compound in colour similar to vermilion, and is obtained by causing sodium or calcium dithionite to act upon antimonious chloride in water, and boiling this mixture, a precipitate being readily deposited; it is a soft, velvety powder, unaltered by the action of air and light, and suited for either oil- or water-colour. This substance may be prepared on a large scale by the following process:—(1) Black antimony sulphide is calcined in a current of air and steam, antimonic oxide being formed as well as sulphurous acid, which may be employed for the preparation of calcium dithionite from soda waste; the antimonic oxide is next dissolved in crude hydrochloric acid. (2) Large wooden tubs which admit of being internally heated by steam, are for $\frac{7}{8}$ths of their capacity filled with the solution of calcium dithionite, and the solution of antimonious chloride is gradually added, the liquid being stirred and heated to about 60°; the reaction soon ensues, and the precipitate having subsided, is thoroughly washed and dried at a temperature not exceeding 50°. There are prepared, on a large scale, by operative pharmaceutical and manufacturing chemists, numerous varieties of antimonial preparations, among which are several sulphides and one oxysulphide, different from the preparation here mentioned.

Antimony Pentasulphide, Sb_2S_5, is obtained by decomposing sodium sulphantimoniate with hydrochloric acid. It is used for vulcanising caoutchouc, for which purpose sodium thiosulphate is added.

COMPOUNDS OF ARSENIC.

Arsenic Acid, according to Schoop, is obtained on the large scale in the following manner. The plant shown (Fig. 367) in plan in $\frac{1}{200}$ of its natural size, consists of the

Fig. 367.



generators, *A*, the absorbent vessels, *B*, a neutralising pan, *C*, and an evaporating pan, *D*. Six generators, *A*, are connected in a suitable manner with five receivers, *v*. From the

last receiver the tube, *r*, leads to the condensing pots, *B*. After the gases have passed through these vessels, they enter the chimney through the tube, *z*. Shortly before this exit, there is a glass tube inserted for observing the colour of the gases. Each generator consists of an earthen vessel, *A* (Fig. 368 in $\frac{1}{30}$ natural size), which has three apertures provided with hydraulic joints. The middle, largest aperture serves to admit a cylindrical stoneware piece, *R*. This piece is perforated like a sieve in its lower half. The arsenical powder is introduced through a smaller opening, *o*, in the cover, whilst the third smaller opening receives the escape-pipe, *n*. The entire stoneware vessel stands in a wooden vat, *H*, and can be surrounded with water, the temperature of which can be regulated at pleasure by means of the steam- or water-pipes, *w* and *d*. The exit pipe, *n*, opens into an earthen vessel, which has essentially the same form as that shown in the condensing-vessel, *B* (Fig. 369, in $\frac{1}{30}$ of its natural size), but having three openings instead of two. The five receivers, *r*, are connected below with the

Fig. 368.

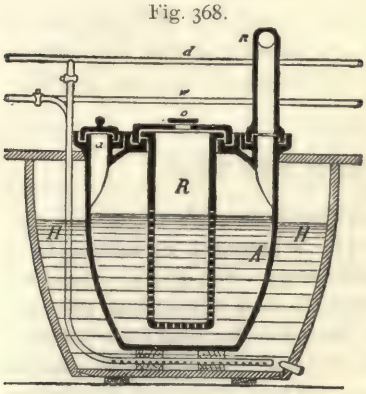


Fig. 369.

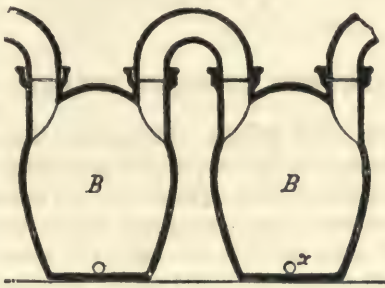
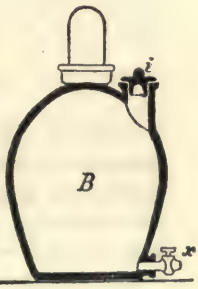


Fig. 370



generators in such a manner that the fumes of a generators have to traverse two to three receivers before arriving at the real condensation-pots, *B*. This arrangement is to prevent loss in case the contents of any generator boil over. The condensing-pots *B* (Figs. 369 and 370), have two large apertures for the gas-entrance- and exit-pipes, as well as a small hole, *i*, for supplying water or dilute nitric acid. Near the bottom there is a smaller opening, *x*, provided with a stoneware cock for letting off nitric acid. The number of the pots is at least 60, to avoid imperfect condensation. In proportion as the contents of the pots nearest the generators, *A*, reach the necessary concentration (sp. gr. 1·32 to 1·35), they are drawn off and replaced by a similar quantity of liquid from the next pot, further from the generators. Whilst water is put into the pot nearest the chimney, nitric acid of sp. gr. 1·34 is drawn off from the first condensing-pot. Into each generator there are poured 180 kilos. nitric acid of sp. gr. 1·35 to 1·40, and 150 kilos. powdered arsenic (so-called white arsenic) are then added. Whilst pure nitric acid has an oxidising action only at high temperatures, crude nitric acid begins to act at common temperatures. The chief reaction sets in at 65° and is most violent at 70°, declining afterwards. Hence, at the outset but little arsenic is added; the water-bath is then heated to 70° by turning in steam, and the remainder of the arsenic is added in small portions. The reaction lasts about sixty hours. At last the heat is raised and the end of the process is ascertained by sampling. A small sample is heated in a porcelain capsule with a little arsenic, over a spirit or gas flame, and if only traces of nitrous fumes escape the operation is broken off. The mass is allowed to cool a little, and it is then drawn with syphons out of the generators, *A*, into the neutralising pan, *C*. If the mixture from all the six generators contains any free nitric acid, arsenic is added, and if it contains an excess of arsenious acid, nitric acid is

added. In either case heat is applied until the escape of gases entirely ceases. The concentration of the arsenic acid is carried to 195° Tw. A continual oversight of the generators is necessary to prevent rising over. If the evolution of gases is very violent, cold water is run from the pipe, *w*, into the vat, *H*, and it is not heated again until the contents are quiet. In general the temperature does not fluctuate much, as the escape of gas absorbs the more heat the more rapid it becomes. Arsenic must never be added in large quantities at once. As much air enters through the loose cover as is needed to oxidise the nitrogen oxides. If the glass tube, *g* (Fig. 367), has a yellow colour near the chimney, there is either too little air in the pots, *B*, or the reaction in *A* is too violent. With careful watching, 75 per cent. of the nitric acid may be recovered.

Besides serving for the production of magenta (a process now generally superseded), sodium arseniate is used as a mordant in tissue printing and in turkey-red dyeing. It is now being superseded in the latter industry by sodium phosphate.

Arsenic acid is tested by dissolving an average sample in a solution of sodium bicarbonate and titrating with solution of iodine. It has been already stated how arsenic acid is tested for free nitric acid or arsenious acid. The commercial product is generally valued according to its sp. gr.

COMPOUNDS OF GOLD, SILVER, AND MERCURY.

Cassius's Purple, Gold Purple.—The preparation which bears this name was discovered by Dr. Cassius, at Leyden, in the year 1663. It is prepared by adding to a solution of gold chloride a certain quantity of tin sesquichloride. Dr. Bolley prescribes the following process:—First, 10·7 parts of the double tin and ammonium chloride are digested with pure metallic tin until the metal is quite dissolved; 18 parts of water are then added, and the liquid mixed with the gold solution previously diluted with 36 parts of water. The result is the throwing down of a purple or black coloured precipitate, about the chemical constitution of which nothing is certainly known. Well-prepared Cassius's purple should contain 39·68 per cent. of gold.

Salts of Gold.—The double salts of gold and sodium chloride ($AuCl_3,NaCl + 2H_2O$), and the corresponding potassium salt ($2AuCl_3,KCl + 5H_2O$), are employed in photography and medicine.

Salts of Silver, Silver Nitrate, Lunar Caustic.—This salt ($AgNO_3$) is now prepared on the large scale by dissolving silver containing copper in nitric acid, evaporating the solution to dryness, and igniting the residue until all the copper nitrate is decomposed. The residue is next exhausted with pure water, the solution filtered and left to crystallise. For medical purposes the crystals are fused, and, while liquid, poured into moulds to form small round sticks. The most extensive use of silver nitrate obtains in photography, a re-crystallised neutral and pure salt being preferred. Under the name of *Sel Clement*, there is now in use in photography a mixture of fused silver, sodium and magnesium nitrates, recommended as preferable to silver nitrate alone. It is stated that the consumption of this salt for photographic purposes amounted, in 1870, to 1400 cwts. for Germany, France, England, and the United States; the money value of this quantity being estimated at £630,000.

Marking Ink.—A large quantity of silver nitrate is also used for the purpose of making indelible ink for marking linen. This ink often consists of two different fluids, one a solution of pyrogallic acid in a mixture of water and alcohol, being intended to moisten the linen previous to writing; the other, or writing fluid, consisting of a solution of ammoniacal nitrate of silver thickened with gum. More recently aniline black has been applied in the marking of linen.*

* The number of marking-inks is now almost endless, and many of them corrode linen.

Mercurial Compounds.—The more important mercurial compounds which are manufactured on the large scale are the following :—

Mercuric Oxide, HgO, is prepared by cautiously heating a mixture of mercuric nitrate with mercury. It is sometimes applied to the iron hulls of steamers to prevent the attachment of mollusca, &c.

Mercuric Chloride.—The substance commonly known as corrosive sublimate is the perchloride of mercury, $HgCl_2$, molecular weight = 135, consisting, in 100 parts, of 73·8 parts of mercury and 26·2 parts of chlorine. It is prepared either by sublimation from a mixture of mercuric sulphate and common salt, or by dissolving the same oxide in hydrochloric acid, and also by boiling a solution of magnesium chloride with the peroxide ($MgCl_2 + HgO = HgCl_2 + MgO$). When sublimed, this salt forms a white crystalline mass, which fuses at 260°, boils at 290°, is soluble in 13·5 parts of water at 20°, and in 1·85 parts of the same liquid at 100°. It is more readily dissolved by alcohol, 1 part of the salt requiring only 2·3 parts of cold and 1·18 parts of boiling alcohol. Mercuric chloride has been industrially employed as a preservative for timber by Kyan, and is used in the manufacture of aniline-red, in dyeing and calico-printing, in etching on steel-plates, and for the preparation of other mercurial salts. Lately, the use of the double salt, $HgCl_2,2KCl$, obtained by boiling potassium chloride with mercury peroxide, has been suggested as a preservative for timber. It should be borne in mind that this preparation of mercury is extremely poisonous and easily absorbed by the skin of the hands.

Cinnabar or Vermilion.—Under this name is designated the mercuric sulphide, HgS, which occurs native in crystalline or compact red-coloured masses, and was known in Pliny's time by the term minium.* The use of mercuric chloride in the manufacture of aniline red, and in dyeing and printing, has practically ceased. The cinnabar, or vermilion of commerce, used as a pigment, is always artificially prepared either by the dry or wet way. By the former process 540 parts of mercury and 75 of sulphur are very intimately mixed. The ensuing black-coloured powder is introduced into iron vessels, and exposed to a moderate heat so as to cause the fusion of the mass, which, after cooling, is broken up and then introduced into earthenware and loosely closed vessels, heated on a sand-bath. The sublimed mass is of a cochineal-red colour, exhibits a fibrous fracture, and yields when pulverised a scarlet powder, which is the more beautiful the purer the materials used in its preparation and the greater the care taken to avoid an excess of sulphur. Some chemists allege that a greatly improved vermilion is obtained if 1 part of antimony sulphide is added to the mixture of sulphur and mercury previously to the sublimation, and the sublimed and pulverised mass placed in a dark room for several months and treated with either dilute nitric acid or caustic potassa. According to Liebig, vermilion is obtained in the wet process by treating the white precipitate of the Pharmacopœia, or *hydrargyrum amidato bichloratum*, with a solution of sulphur in ammonium sulphide. Hofmann considers white precipitate to be ammonium chloride, in the ammonium of which 2 equivalents of mercury have taken the place of 2 equivalents of hydrogen; formula $N\begin{cases}H_2\\Hg_2.\end{cases}$ Other chemists, again, hold different views as to the constitution of this body, which has been used in medicine since, if not before, the time of Paracelsus. Vermilion is generally obtained by precipitating a solution of corrosive sublimate in ammonia with a solution of sulphur in ammonium sulphide; or, according to Martius, by agitating, in a suitable vessel, 1 part of sulphur of mercury, and 2 to 3 of a concentrated solution of liver of sulphur. According to Brunner's method, by which decidedly the finest vermilion is obtained, 114 parts by weight of sulphur and 300

* Red lead, afterwards called minium, was, as far as it appears, unknown to the ancients, being first prepared by the Arabs and Saracens.

parts by weight of mercury are mixed, with the addition of a small quantity of caustic potassa solution, and incorporated by being shaken by machinery. The resulting black compound is next treated with a solution of 75 parts caustic potassa in 400 parts of water, and heated on a water-bath to 45°. The mixture assumes a scarlet-colour after a few hours, and as soon as this is apparent the semi-liquid mass is poured into cold water, next collected on filters, washed, and dried. The vermilion of commerce is often adulterated with red lead, iron peroxide, chrome lead, and, more frequently, with from 15 to 20 per cent. of gypsum. These adulterations are, however, readily detected, as they are left behind when the vermilion is sublimed. Red lead, one of the most usual adulterations of vermilion, can be readily detected either by treating a small quantity of the suspected sample with nitric acid, when, in consequence of the formation of puce-coloured lead peroxide, the mass assumes a brown colour, or by the addition of hydrochloric acid, when chlorine is given off. Pure cinnabar is completely and readily soluble in hydrosulphuret of sodium sulphide (NaSH).

Red lead, or antimonial cinnabar, is sometimes passed off as vermilion by steeping it in a solution of eosine. If such a sample is digested in alcohol, the eosine is dissolved away, and the red lead, &c., is revealed.

COMPOUNDS OF COPPER.

Copper Sulphate, Blue Vitriol, Blue Stone.—This salt is met with naturally in kidney-shaped masses, or as an outer covering of minerals containing copper, as well as in solution, as referred to under Cementation-copper. Copper sulphate, blue- or Cyprus-vitriol crystallises in the shape of triclinohedrical blue-coloured crystals, soluble in two parts of hot and four of cold water, and insoluble in alcohol. 100 parts of the salt contain—

Sulphuric acid . . .	32·14
Oxide of copper . . .	31·79
Water	36·07

Formula—$CuSO_4 + 5H_2O$.

Preparation of Blue Vitriol.—Pure copper sulphate is obtained by heating metallic copper with concentrated sulphuric acid; the metal is oxidised by a portion of the oxygen of the acid, while sulphurous acid escapes:

$$(Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2).$$

If the metal is previously converted into copper oxide by exposure to a red heat, only half the quantity of sulphuric acid is required. Copper sulphate is manufactured on a large scale by any of the following processes:—1. By the evaporation of cementation water until crystallisation is attained. 2. By heating sheets of copper in a reverberatory furnace to the boiling-point of sulphur; a quantity of that element being then thrown in, and the flues and other openings closed, the effect is the formation of copper sulphide (Cu_2S), which is converted by a comparatively low heat and the action of the oxygen of the air into sulphate ($Cu_2S + 5O = CuSO_4 + CuO$). The mass is next placed in a suitable vessel, and as much sulphuric acid is added to it as is sufficient to saturate the oxide of copper. The clear solution, having been decanted from the insoluble residue, is set aside for crystallisation. 3. By treating the crude copper obtained by smelting the ores, and containing about 60 per cent. of metal, with sulphuric acid. The resulting solution is evaporated in leaden vessels, and the clear liquid left to crystallise in copper pans. From the mother liquor of the crystals metallic copper is precipitated by means of iron, because the presence of a large quantity of iron sulphate renders this mother liquor unfit for the further making of blue vitriol. This method of obtaining copper sulphate is the least expensive,

but the salt is not quite pure, containing, according to M. Herter's analysis of Mansfeld blue vitriol, about 3 per cent. of iron sulphate, and 0·083 per cent. of metallic nickel. Very frequently the scraps and refuse of copper-smithies, copper-scale, and other residues of that metal, are used in preparing copper sulphate. 4. At Marseilles, malachite is dissolved in sulphuric acid to obtain blue vitriol. 5. In Norway, iron pyrites containing copper are roasted and treated with water, the copper contained being precipitated with sulphuretted hydrogen, and the copper sulphide, when dry, converted into sulphate by exposure to a gentle heat. 6. Large quantities of copper sulphate are obtained as a bye-product of silver-refining (especially when silver is treated for the purpose of extracting the gold it contains), by boiling—usually silver coins, chiefly Mexican and Peruvian dollars—with strong sulphuric acid; silver sulphate and, as the coins contain some copper, the sulphate of that metal, are formed, while the gold is left as an insoluble substance. The silver is reduced to the metallic state ($Ag_2SO_4 + Cu = CuSO_4 + 2Ag$) by means of sheets of copper placed in the acid solution, which is previously diluted, and which, after having been decanted from the sediment of spongy metallic silver, yields on evaporation a very pure copper sulphate. 7. Copper sulphate is also obtained as a bye-product of the hydrometallurgical process of extracting silver, or Ziervogel's process. In order to separate the iron sulphate from the crude blue vitriol, as obtained at copper-smelting works from various cupriferous refuse, the crude salt is roasted so as to bring about a partial decomposition. By this means the irons ulphate is decomposed, and the oxide of that metal formed is insoluble in water. The saline mass is dissolved in water, and the clear solution, decanted from the sediment, evaporated to crystallisation. According to Bacco's plan, the crude blue-vitriol is dissolved in water, and copper carbonate added to the solution, to cause the precipitation as oxide of all the iron present, while an equivalent quantity of copper oxide is dissolved and converted into sulphate. The purified copper sulphate solution having been filtered is evaporated and left to crystallise.

Double Vitriol.—Under the name of double vitriol, a mixture of the copper and iron sulphates crystallised together, and sometimes containing white vitriol, is met with on the Continent. The Salzburg vitriol, known by the brand of a double eagle, contains about 76 per cent., the Admont 83 per cent., and the double Admont 80 per cent. of ferrous sulphate. Of later years, however, these vitriols have been less in demand.

Applications of Blue Vitriol.—As the base of the pigments obtainable from copper, the sulphate is very frequently used, and should be pure, or at least free from iron and zinc sulphates. Blue vitriol also serves for the manufacture of copper acetate, for bronzing iron, for bringing out the colour of alloys of gold. It is used in dyeing and printing in various ways, for galvano-plastic purposes, and during the last twenty years large quantities of this salt have been sent to Mexico and Peru to be applied in the American amalgamation-process of extracting silver.

Copper Pigments.—(*Brunswick Green, Bremen Blue or Green, Casselmann's Green, Scheele's Green, Oil Blue, Schweinfurt Green, Verdigris.*).—*Brunswick Green.*—Under this name several compounds of copper are applied as oil-paints. The pigment now chiefly in use bearing this name is basic copper carbonate ($CuCO_3 + CuH_2O_2$), an imitation of mountain- or mineral-green, and obtained from either finely pulverised malachite or the sediment often met with in cupriferous cementation liquids. Brunswick green is prepared on a large scale by the decomposition of ferrous sulphate by means of either sodium or calcium carbonate, and in other cases by the decomposition of copper chloride by means of a carbonated alkali. The ensuing precipitate is washed with boiling water, and afterwards mixed with a smaller or larger quantity of barium sulphate, zinc-white, or gypsum, and frequently with Schweinfurt

green (copper aceto-arsenite) in order to obtain the desired hue. Another variety of Brunswick green, rarely met with in the present day, appears to be a kind of artificially prepared atacamite, a copper oxychloride, the formula of which is, according to Rittthausen, $CuCl_2.3Cu(HO)_2$.

Bremen Blue or Bremen Green.—These substances are essentially hydrated copper oxide, and are met with as a very bright spongy blue mass with a greenish hue. The value is greater according to the finer blue colour and loose spongy texture. When used with water, gum, or glue, this pigment yields a bright blue colour, hence its first name; but when it is mixed with linseed oil, the blue colour turns within twenty-four hours to green, in consequence of the saponification of the copper oxide, which becomes oleate, palmitate, and linoleate of that base. Bremen green occurs in various hues, obtained by mixing the precipitate with well-cleansed gypsum. At the present time the pigment is generally obtained from copper oxychloride ($CuCl_2 3CuO + 4H_2O$). This preparation may be made in various ways, provided care be taken that the light green paste—technically known as oxide—contains no cuprous chloride ($CuCl_2$). Gentele's method is as follows:

1. 112·5 kilos. of common salt, and 111 kilos. of copper sulphate, both free from iron, are ground together with sufficient water to promote reaction. 2. 112·5 kilos. of old copper sheeting is cut into pieces a square inch in size, and placed with water acidulated with sulphuric acid in rotating casks so as to remove all rust, oxide, and oxychloride from this metal, which is next washed with water. 3. The clean metal thus obtained is next placed in what are known as oxidisation-closets and covered for a thickness of half an inch with the paste mentioned above. A mutual action, aided by that of the atmosphere, is set up, the result being that the copper chloride first takes up copper, becoming cuprous chloride; this in its turn takes up oxygen from the atmosphere and water, and thus becomes converted into the green-coloured insoluble hydrated copper oxide, the action being greatly aided by the turning over of the mass with a copper spade every two or three days. As the treatment of cuprous chloride with alkalies or alkaline earths gives rise to the separation of red or yellow coloured suboxide, the mass should not, on being tested and previous to further operations, yield even the faintest indication of the presence of suboxide, since the slightest trace would spoil the hue of the pigment to be obtained; consequently, in some works the pasty mass is left for years before it is used for further operations. The action is accelerated by causing the mass to become dry before turning it over with a spade, the consequence being that the air gets thorough access, and a complete oxidation is obtained in from three to five months' time. The mass is then cleaned with the smallest possible quantity of water, and is thus separated from the non-oxidised metallic copper. 4. To about 6 gallons of this cleaned material are added 6 kilos. of hydrochloric acid, and this mixture is allowed to stand for about two days. 5. Into a tank or tub —the blue tub—are poured 15 gallons of clear colourless potassa lye. This having been done, the acid mixture is first diluted with 6 more gallons of water, and then, as rapidly and expeditiously as possible, poured into the blue tub, the mixture being continuously stirred. The result of this last operation is that the previously basic copper compound, converted by HCl into neutral cupric chloride, is, when brought in contact with the potassa, converted into blue-coloured copper oxyhydrate or Bremen blue, while potassium chloride is also formed. 6. After the mass has become pasty, it is left to stand for a couple of days, and then thoroughly washed by decantation to remove the potassium chloride. The cupric oxyhydrate is then put on cloth filters, kept moist, and exposed to the air for some time. It is next dried at a temperature of from 30° to 35°, since at a higher temperature the hydrate of the oxide by losing its water becomes blackish-brown coloured. It is clear that Bremen blue can be differently obtained, but these differences of preparation do not bear so much upon the

precipitation of the hydrated oxide as upon the means of obtaining copper chloride; these means may of course be varied in many ways; for instance, by causing a mixture of common salt, dilute sulphuric acid, and copper scraps to act upon each other, the mass being afterwards exposed to the action of the air; by the action of hydrochloric acid upon copper and its oxide; or by partly decomposing neutral copper nitrate by means of sodium carbonate. In this case a precipitate of copper carbonate is formed, which, while giving off its carbonic acid, becomes converted into a basic copper nitrate ($CuN_3O_6 + CuH_2O_2$), deposited as a heavy green powder. A solution of zinc-oxide of potassa (solution of zinc-white in caustic potassa) is next added, the result being the formation of a deep blue pigment, very spongy and very *covering* (a technical term in use by painters), consisting of copper zincate with a small quantity of basic copper nitrate. A magnesia Bremen blue is obtained by the precipitation of a solution of the magnesium and copper sulphates, to which some cream of tartar is added by means of potassa, care being taken to pour the saline solution into the alkaline, and to keep an excess of the latter.

Casselmann's Green.—Dr. Casselmann discovered this pigment, a beautiful green free from arsenic. It is prepared by mixing together boiling solutions of copper sulphate and an alkaline acetate; the resulting precipitate is a basic salt of copper ($CuSO_4 + 3CuH_2O_2 + 4H_2O$). After drying, this salt is, next to Schweinfurt green, the finest of all colours obtained from copper, and being free from arsenic, is highly commendable, though poisonous, like most preparations of copper, especially the acetates.

Mineral Green and Blue.—This pigment, also known as Scheele's green, is not so frequently used now as formerly. It is essentially a mixture of hydrated copper oxide and arsenite, and does not cover very well. It is prepared by dissolving 1 kilo. of pure copper sulphate in 12 litres of water, to which is added, with constant stirring, a solution of 350 grammes of arsenious acid and 1 kilo. of purified potash (carbonate) in 8 litres of water. The resulting grass-green coloured precipitate is washed with boiling water and dried. Another pigment, sometimes known as mineral green, is obtained from malachite, or basic hydrated copper oxide. By the term mineral blue is generally understood a kind of Berlin blue, rendered less deep coloured by the addition of pipe-clay or other white-coloured powders, but the terms also applies to a pigment formerly obtained by grinding and washing the purest pieces of copper lazulite, a mineral ($2CuCO_3 + CuH_2O_2$) found in the Tyrol and near Lyons. This pigment is artificially obtained in France, Holland, and Belgium, by precipitating a solution of copper nitrate with caustic lime or caustic potassa, and afterwards mixing the previously washed precipitate with chalk, gypsum, or heavy spar. The pigment is sent into the trade for use chiefly as a water-colour. Under the name of lime blue a similar preparation occurs in quadrangular lumps, obtained by precipitating a solution of 100 parts of copper sulphate and 12½ parts of sal-ammoniac with a milk of lime containing 30 parts of caustic lime. The precipitate is a mixture of hydrated copper oxide and calcium sulphate, according to the formula, $2CaSO_4.2H_2O + 3CuOH_2$. This pigment exhibits a purer tint than Bremen blue, but though it covers pretty well as a water-colour, it is almost useless as an oil-colour.

Oil Blue.—A pigment which, when ground with oils and varnishes, yields a beautiful violet-blue, and is essentially composed of copper sulphide, (CuS), there being employed in its manufacture either the native mineral, known as cupreous indigo, or an artificially prepared sulphide, obtained by fusing finely divided metallic copper with hepar sulphuris, a mixture of several potassium sulphides. The fused mass is treated with water, and the copper sulphide remains in small blue-coloured crystals, which, after drying, are pulverised and mixed with oil.

Schweinfurt Green or Emerald Green.—This pigment is by far the most beautiful, but

also the most poisonous, of all green-coloured copper pigments. In Germany this substance is known under a number of aliases derived from the peculiar depth of hue as modified in various manufactories by means of barium sulphate, lead sulphate, and chrome-yellow. The constitution and mode of preparation of this pigment remained, at least on the Continent, a trade secret, until the researches of MM. Braconnot and Liebig made the particulars known. According to Ehrmann, pure emerald or Schweinfurt green is a copper aceto-arsenite, $Cu(C_2H_3O_2)_2.3Cu(AsO_2)_2$; in 100 parts—oxide of copper, 31·29; arsenious acid, 58·65; acetic acid, 10·06. Wagner states that this formula is only empirical, because a portion of the copper is present as suboxide, and a portion of the arsenic as arsenic acid.

According to Ehrmann's statement, this pigment is prepared by first separately dissolving equal parts by weight of arsenious acid and neutral copper acetate in boiling water, and next mixing these solutions while boiling. There is immediately formed a flocculent olive-green coloured precipitate of copper arsenite, while the supernatant liquid contains free acetic acid. After a while the precipitate becomes gradually crystalline, at the same time forming a beautifully green pigment, which is separated from the liquid by filtration, and after washing and carefully drying is ready for use. The mode of preparing this pigment on a large scale was originally devised by Braconnot, as follows:—15 kilos. of copper sulphate are dissolved in the smallest possible quantity of boiling water and mixed with a boiling and concentrated solution of sodium or potassium arsenite, so prepared as to contain 20 kilos. of arsenious acid. There is immediately formed a dirty greenish-coloured precipitate, which is converted into Schweinfurt green by the addition of some 15 litres of concentrated wood vinegar. This having been done, the precipitate is immediately filtered off and washed. It thus appears that the preparation of this pigment aims first at the least expensive preparation of neutral copper arsenite, which is next converted into aceto-arsenite by digesting the precipitate with acetic acid. The pigment is available as a water- and an oil-colour, but does not cover very well in oil, although it dries rapidly. The colour cannot be used for mural painting, as the lime absorbs the acetic acid, leaving a yellowish-green copper arsenite. The Schweinfurt green consists of microscopically small crystals; if these crystals are pulverised, the colour, previously grass-green, becomes paler. Air and light do not affect this pigment, which is insoluble in water, but becoming, when boiled with it for a length of time, brown-coloured, probably in consequence of the loss of some acetic acid. It is a well-known fact that paper-hangings containing this pigment, and pasted on damp walls, cause the inmates of the rooms to suffer from headaches, due in all likelihood to volatile arsenical emanations, among which is hydrogen arsenide. The use of this pigment is very limited.

Copper Stannate.—This preparation, also known as Gentele's green, is obtained by precipitating a solution of copper sulphate with sodium stannate, washing and drying the precipitate, which forms a beautifully green copper pigment, innocuous, at least as compared with the foregoing.

Verdigris.—Under this name we meet in commerce with a neutral and a basic copper acetate; the one, a crystalline substance, is $Cu(C_2H_3O_2)_2.H_2O$, a salt formerly only prepared in Holland, and designated as "distilled verdigris," in order to mislead as to its mode of manufacture.

The basic salt, blue verdigris, is chiefly prepared at and near Montpellier, by employing the marc of grapes, the skin and stems of the bunches after the juice has been squeezed out, which readily forms acetic acid by fermentation. Into the marc are placed sheets of copper previously moistened with a solution of copper acetate. The metal becomes coated with a layer of verdigris, which is removed by scraping. It is next kneaded with water, after which the paste is put into leathern bags and pressed,

so as to obtain rectangular cakes. The metal is again treated in the same manner until it is entirely converted into basic verdigris, having a blue colour, and known as French verdigris. Formula—$Cu(C_2H_3O_2)_2.Cu(OH)_2.5H_2O$. A green-coloured verdigris is obtained at Grenoble and elsewhere by submitting sheets of copper to the action of vapours of vinegar, or by placing the metal between pieces of coarse flannel, soaked with that liquid in a warm place. The formula of the substance thus produced is—$Cu(C_2H_3O_2)_2.2Cu(OH)_2$.

Neutral copper acetate first made by the Saracens in Southern Spain, and since the middle of the fifteenth century by the Dutch, is now obtained either by—1. Dissolving the basic salt in acetic acid. 2. Or by the double decomposition of copper sulphate and lead acetate:—$CuSO_4 + Pb(C_2H_3O_2)_2 = PbSO_4 + Cu(C_2H_3O_2)_2$.

By the first method the basic acetate is dissolved in 4 parts of acetum destillatum (purified vinegar) or in wood vinegar, the liquid being placed in a copper cauldron and heat applied. The clear liquid is decanted, and then evaporated in copper pans until a saline crust makes its appearance, when the fluid is transferred to wooden vessels provided with thin laths serving as a solid nucleus for the crystals. According to the second plan, the solutions of the two salts are mixed, the liquid decanted from the sediment of lead sulphate, and next evaporated, after the addition of some acetic acid, until a crust of the salt is formed. Instead of lead acetate, the calcium and barium acetates are now used. The neutral copper acetate is met with in commerce in "bunches" (*grappes*), consisting of deep green-coloured, non-transparent crystals, soluble in 13·4 parts of cold, in 5 parts of hot water, and in 14 parts of boiling alcohol. This salt, like the basic acetates, is highly poisonous.

Applications of Verdigris.—Both basic and neutral are employed as oil- and water-colours. In Russia, verdigris, mixed with white-lead, is frequently used as an oil paint, the result being the formation of copper carbonate and basic lead acetate. The former of these substances yields with the undecomposed white-lead a bright blue colour, which, after painting, turns to a peculiarly fine green, the usual colour of the iron roofs of the houses in Russia, more especially in Moscow and the interior of the country. In Holland the same mixture is frequently applied as a paint to outdoor woodwork, of which it is an excellent preservative. Verdigris is sometimes further applied in the preparation of other copper colours—for instance, Schweinfurt green; also in dyeing and calico-printing, though less commonly than formerly; in gilding (*see* Gold). The neutral salt was formerly used in the preparation of acetic acid.

Egyptian Blue, a blue pigment known to the Egyptians from time immemorial, and lately rediscovered, is obtained by fritting a mixture of sand (free from iron) 70 parts, copper oxide 15 parts, chalk 25 parts, and sodium carbonate 6 parts.*

COMPOUNDS OF ZINC AND CADMIUM.

Zinc-white.—Under this name there has during the last fourteen years been brought into the market anhydrous white zinc oxide, applied instead of white-lead as a pigment. Zinc-white is prepared for this purpose by oxidising metallic zinc in fireclay retorts, placed to the number of 8 to 18 in a reverberatory furnace. As soon as these retorts are at a bright white-heat, cakes of zinc are placed in them, and the vapours of the metal on leaving the retort are brought into contact with a current of air heated to 300°; oxidation results, and the oxide, a very loose, snow-white, flocculent material, is carried by the current of hot air into condensing chambers, and gradually

* Concerning these preparations and pigments, the reader may consult, A. H. Church, *Chemistry of Paints and Painting*, London, Seeley & Co.; and Gentele, *Lehrbuch der Farbenfabrikation*, Brunswick, Vieweg & Son.

deposited. The oxide thus prepared is immediately fit for use; it is of a pure white colour, and very light. Zinc-white is also prepared by exposing metallic zinc to the action of superheated steam, hydrogen being at the same time evolved, and used for illuminating purposes, as at Narbonne, St. Chinian, Cèret, and a few other places, where it is known as platinum-gas, because the flame is used for imparting a white heat to small coils of platinum wire, thus producing a very steady and highly pleasant light. As regards the use of zinc-white as a pigment, it is rather more expensive than white-lead, yet according to some it is a better covering material in the surface proportion of 10 to 13, that is to say, 13 parts by weight of zinc-white cover as much space as 10 of white-lead: moreover, zinc-white is not affected by sulphuretted hydrogen. Like white-lead, this compound may be mixed with other pigments. By mixing Rinmann's green with it a green colour may be obtained; blue with ultramarine; lemon-yellow with cadmium orange-yellow (cadmium sulphide).

A zinc carbonate has been proposed as a pigment; it is prepared by precipitating solution of zinc sulphate with ammonium carbonate.

Zinc-white is often prepared directly from its ores; the roasted ores are heated upon the grate of a furnace and when fully ignited submitted to a current of air passed underneath the grate. The escaping vapours are again strongly heated along with a current of air and condensed in lead chambers. Schnabel digests zinc dust with ammonium carbonate in leaden vessels. The great advantage of zinc-white is that it is not blackened by sulphur-gases, and that it is less injurious to workmen than white lead.

White Vitriol, Zinc Sulphate.—Zinc-vitriol ($ZnSO_4 + 7H_2O$), zinc sulphate or white vitriol, is found as a native mineral, as a product of the oxidation of zinc blende; it is also prepared by dissolving zinc in dilute sulphuric acid, and by roasting native zinc sulphide. This vitriol occurs in white agglomerated crystals and in small acicular-shaped crystals, as purified zinc sulphate; it is used as a "dryer" in oil paints and varnishes; as a mordant in dyeing; for disinfecting purposes, and sometimes as a source of oxygen, since, on being submitted to a red heat, it gives off sulphurous acid and oxygen, zinc oxide remaining.

Zinc Chromate.—This preparation, obtained by precipitating a solution of zinc sulphate with potassium bichromate, is a very fine yellow-coloured powder, used now and then in pigment printing, because it is soluble in ammonia, and thrown down again as a powder insoluble in water when that menstruum is volatilised. A basic zinc chromate is used as a pigment in the paint trade.

Zinc Chloride.—This compound of zinc, $ZnCl_2$, is obtained either by dissolving zinc in hydrochloric acid, or more cheaply by causing the hydrochloric acid gas given off in manufacturing soda to act upon native zinc sulphide. By this action sulphuretted hydrogen is formed, which can be burned to produce sulphurous acid for the sulphuric acid chambers. The solution of zinc chloride thus obtained is evaporated to the consistency of a syrup.

Anhydrous zinc chloride is obtained by heating an intimate mixture of dried zinc sulphate and sodium chloride; zinc chloride is formed which sublimes, and sodium sulphate which is left behind ($ZnSO_4 + 2NaCl = Na_2SO_4 + ZnCl_2$). This anhydrous chloride may be sometimes advantageously used instead of strong sulphuric acid, for instance, in rape and colza oil refining, and perhaps, although it would be more expensive and less manageable, in the manufacture of garancine from madder. This chloride has of late been employed instead of sulphuric acid in the manufacture of stearic acid, and in the preparations of ether and parchment paper. Zinc chloride in a strong and crude solution is largely and very successfully used for preserving timber; in paper-making for the decomposition of bleaching powder, for bleaching the half-stuff and rags, and also in sizing paper. The disinfectants sold as Sir William Burnett's

Fluid and Drew's Disinfectant are solutions of zinc chloride. The salt used in soldering iron, zinc, pewter, &c., is a compound of zinc and ammonium chlorides ($2NH_4Cl + ZnCl_2$); its solution is obtained by dissolving 3 parts by weight of zinc in strong hydrochloric acid, and adding after the solution is complete an equal weight of sal-ammoniac. Zinc oxychloride, obtained by mixing zinc oxide with a concentrated solution of zinc chloride, or with solutions of iron or manganese chlorides, has been recently proposed by M. Sorel as a plastic mass suited for stopping hollow teeth.

Cadmium Yellow (*Jaune brilliant*; CdS).—This pigment is prepared by the action of sulphuretted hydrogen upon soluble cadmium salts; a little free acid should be present. The hotter and more concentrated the solution, the more the product inclines to a red.

COMPOUNDS OF LEAD.

Lead Oxide, PbO, is used in used in the arts as massicot or as litharge.

Massicot.—Massicot, or yellow lead oxide, occurs as a yellow or ruddy-coloured powder, obtained either by heating lead carbonate or nitrate, or by calcining metallic lead on the hearth of a reverberatory furnace. Before lead chromate was known, massicot was used as a yellow pigment. At a red heat this substance fuses and becomes glassy. In most instances it is not a pure lead oxide, but is mixed with lead silicate, the fact being that lead oxide at a red heat strongly attacks any material containing silica, dissolving the silica and combining with it.

Litharge.—Litharge is a fused crystalline lead oxide, and is obtained as a bye-product of the separation of silver from lead in the process described under Silver. Litharge always contains a larger or smaller quantity of copper oxide, antimony oxide, traces of silver oxide, and, according to Dr. Wittstein, metallic lead, varying in quantity from 1·25 to 3·10 per cent. The copper oxide can be removed by digesting the litharge with a cold solution of ammonium carbonate. Litharge absorbs carbonic acid from the atmosphere, combines at a higher temperature with silica, forming with it a readily fusible glass, is soluble in acetic and nitric, and also in very dilute hydrochloric acids, and is equally soluble in boiling solutions of caustic potassa and soda. It is insoluble in ammonium carbonate and in the potassium and sodium carbonates. Litharge is largely used, entering into various compounds for glass, so-called crystal-glass, flint-glass, strass for imitating jewels, for glazing pottery and earthenware, as a flux in glass and porcelain staining, for the preparation of boiled linseed and poppy-seed oil, for the preparations of lead plaster, putty, minium, red-lead, and lead acetate. A solution of lead oxide in caustic soda lye is employed in the preparation of sodium stannate; this solution is also used for imparting to combs and other toilet articles made of horn the appearance of tortoiseshell or of buffalo-horn. A very dilute solution is used as a hair-dye, and in metallochromy to produce iridescent colours on brass and bronze.

Minium. Red Lead.—Red lead is a combination of lead oxide with peroxide, the formula being Pb_3O_4. Red lead of excellent quality is largely manufactured near Newcastle-on-Tyne, by carefully heating lead oxide in a reverberatory furnace expressly built for that purpose, the access of air being limited so as to prevent the fusion of a portion of the oxide to litharge which cannot then be converted into minium. Sometimes metallic lead is oxidised in a reverberatory furnace, the process, as, for instance, at Shrewsbury, being so arranged that at the hotter places of the furnace massicot, and at the cooler red lead, is produced. The finest coloured minium, or Paris-red, is obtained from lead carbonate by the same method. According to Burton's plan, lead sulphate is heated with Chili saltpetre, and after the mass has been exhausted with water the red-lead is left, while sodium sulphate and nitrite are dissolved. Red lead is used

for a variety of purposes, many similar to the applications of lead oxide. Besides being applied as a cement, when mixed with linseed-oil and mastic, for the flanges of steam-pipes, it chiefly enters the market as a pigment, being for that purpose either mixed with water or with linseed-oil, in both instances covering extremely well.

Lead Peroxide.—When red-lead is treated with moderately strong nitric acid, there are formed lead nitrate and peroxide of that metal, PbO_2, a brown-coloured powder largely used in the composition of the phosphorus mixture for lucifer matches. The mixture known in lucifer match works as oxidised minium, is a dried composition, consisting of lead nitrate, lead peroxide, and undecomposed red-lead, and obtained by drying a magma of minium and nitric acid.

White-lead, basic lead carbonate, $2PbCO_3.Pb(OH)_2$, or rather hydrate carbonate, is commercially known as of the Dutch, French, or English manufacture, according to the method employed. The Dutch process for making white-lead is founded on the fact that when metallic lead comes in contact with the vapours of acetic acid, carbonic acid, and oxygen, at a sufficiently high temperature, the metal is converted into basic lead carbonate. It is quite evident from this brief statement that the chief conditions being fulfilled, the methods of operation may be more or less varied. In Holland, Belgium, and some parts of Germany, the lead—as pure as possible and free from silver, which, even in small quantities greatly impairs the good colour of the white-lead—is cast into thin strips, which are wound in a spiral P, Fig. 371, in coarse earthenware pots, A (Fig. 371). Common vinegar, C, is poured into the lower part of

Fig. 371.

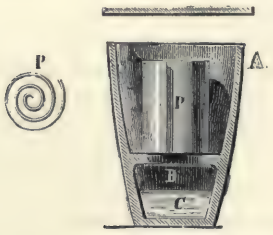


Fig. 372.



these pots, some beer-yeast being added. The lead is supported and placed on a perforated piece of wood, B, so as to prevent direct contact with the vinegar. After this the pots are covered with leaden plates and buried (see Fig. 372) in a mass of horse-dung or spent-tan and dung. The fermentation of the dung causes the requisite increase of temperature, and the vinegar evaporating, aided by the oxygen of the air, converts the lead into basic acetate, which, in its turn, is converted into basic lead carbonate by the carbonic acid resulting from the fermenting manure. This rather clumsy process has given place in Germany to the chamber method, consisting essentially in the following arrangement. Instead of the pots being made the receptacles for the lead, the strips of that metal are bent and suspended on a series of laths run lengthwise through the chamber, on the floor of which is placed a layer of spent tan, marc of grapes, or other fermentable material, saturated with vinegar. An improvement upon this arrangement is to have the chamber constructed with a double flooring, one water-tight, the other a light planking perforated so as to admit of the vapours of vinegar being carried into the compartment. The action upon the lead is in each case the same; it is converted chiefly into white-lead, and this crude product is purified from any adhering lead acetate by washing with water before being brought into the market. There is still in use in this country a modification of the method practised by the Dutch, who, by-the-by, are not the inventors of white lead manufacture, the true origin being Moorish,

the trade being successfully carried on by these semi-savages* in Southern Spain, whence the Dutch brought over the art in the sixteenth century to Holland. The modification consists in the following arrangement :—Granulated lead is first moistened with about 1·5 per cent. of vinegar, the metal being previously placed on hurdles in a wooden box, the interior of which is heated by means of steam to 35°, some steam being introduced to keep the lead moist. If care is taken to supply carbonic acid, after from ten to fourteen days the operation is finished, and the product having been lixiviated with water and dried, is ready for use.

English Method of Manufacturing White Lead.—According to this plan the metal is melted in a large iron cauldron, and then made to flow on the hearth of a reverberatory furnace, so as to convert the lead, by proper access of air, into litharge, which is obtained in a very finely divided state by a peculiar arrangement of the furnace. The hearth is constructed with a gutter, into which the fusing mass flows, and the sides or walls of the gutter are perforated to admit of the passage of the molten litharge, while the heavier metal sinks to the bottom. The litharge is next mixed with $\frac{1}{100}$ of its weight of a solution of lead acetate, and then placed in a series of closed troughs communicating with each other and admitting of the passage of a current of impure carbonic acid, obtained by the combustion of coke in a furnace provided with a blast to give an impulse to the gas. The litharge is continually stirred by machinery to accelerate the absorption of the carbonic acid gas. White lead made by this process covers very well, and is preferred to that prepared by the wet method. We may mention in passing that it is the custom in this country to bring white lead into the market ground with linseed oil to a thick paste, packed in strong oaken kegs or in iron canisters.

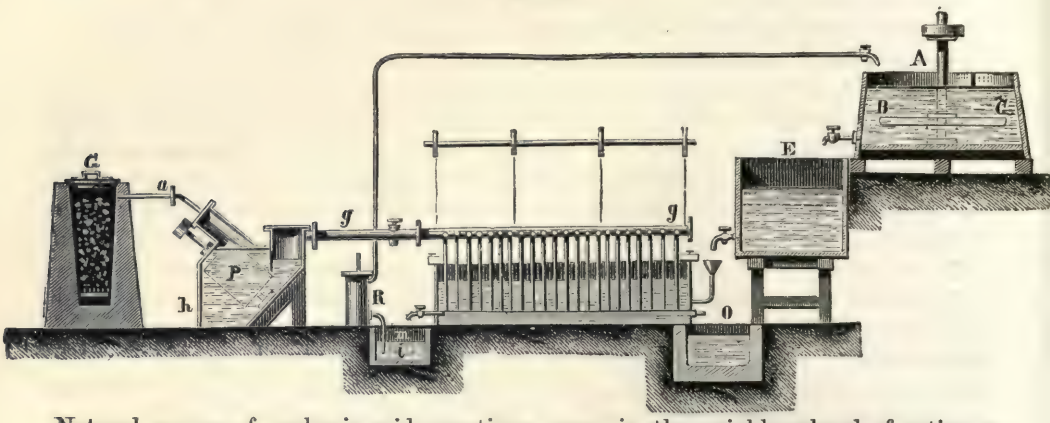
French Method of Preparing White Lead.—This method, invented by MM. Thénard the elder, and Roard, is not only generally adopted in France but in all countries where it is desired to carry out a really sound and rational plan of white lead manufacture. The method is as follows :—Litharge is dissolved in acetic acid to obtain a solution of basic lead acetate—$Pb(C_2H_3O)_2O_2 + Pb(OH_2)$, and through the solution a current of carbonic acid gas is passed. Two molecules of oxide of lead are converted into white lead, while neutral lead acetate remains. Litharge is again added to the solution of this salt, and, by digestion, more lead subacetate is obtained, which is applied as just described.

Apparatus used in White Lead Manufacture at Clichy.—The machinery and contrivances at Clichy, near Paris, for effecting the method just explained, are exhibited in Fig. 373. In the tub, A, the litharge is dissolved in acetic acid. B C is a stirrer, moved by means of the shaft shown in the engraving, bearing at the top a pulley for the strap. The solution of basic lead acetate can be run off through the tap into the vessel, E, made of copper and tinned inside, the object being to let the impurities the solution might contain subside. From E the fluid is led into the decomposition vessel constructed with 800 tubes, which pass from the top to a depth of 32 centimetres beneath the level of the fluid. These tubes are in communication with the main pipe, *gg*, which also communicates with the washing apparatus, P, answering the purpose of purifier for the carbonic acid gas generated in the small lime-kiln, G, by the ignition of a mixture of parts by bulk of chalk and 1 part by bulk of coke with sufficient access of air. The decomposition of the basic lead acetate being finished in from twelve to fourteen hours, the supernatant liquor, neutral lead acetate, is run off into the vessel, *i*, and the semi-fluid magma of white-lead passes into O. The pump, R, serves to again convey the neutral acetate to the tank, A, and the operation is re-commenced. The white lead in O is well washed—the first wash-water being conveyed back to the tank, A, and

* How the builders of the Alhambra and the inventors of the rotation of crops can be called "semi-savages," is an unsolved problem.—EDITOR.

after drying is ready for use. In order to obtain the carbonic acid cheaply, it has been proposed to ignite a mixture of chalk or limestone, charcoal, and peroxide of manganese ($CaCO_3 + C + 3MnO_2 = Mn_3O_4 + CaO + 2CO_2$.) Where admissible, the carbonic acid resulting from the fermentation of beer-wort, or of distillery-wash, may be applied.

Fig. 373.



Natural sources of carbonic acid sometimes occur in the neighbourhood of active or extinct volcanoes; and near Brohl, close to the Laacher Sea in Rhenish Prussia, a locality well-known to tourists, a very plentiful and continuous supply of carbonic acid is naturally obtained and actually applied for the purpose under consideration.

Among the very various suggestions for improved methods of making white lead, and for which an enormous number of patents have been taken out, especially in this country and in the United States, we briefly mention the following:—Button and Dyer first slightly moisten litharge with water, next mix it with a small quantity of a solution of lead acetate, place the mixture in a stone trough, agitating and passing hot carbonic acid over it. Pallu (1859) causes finely-divided lead to be thrown with great force, by means of a centrifugal machine, on an inclined plane, care being taken to moisten the lead with acetic acid. After the lapse of an hour, the finely divided lead is converted into acetate and carbonate. A solution of lead acetate is then poured over the mass, and the lead acetate it contains is dissolved, while the white lead is carried into a tank, and there forms a deposit. Grüneberg (1860) prepares white lead by submitting granulated lead to the simultaneous action of air, acetic and carbonic acid, aided by the rapid motion of the metal. From private information obtained from the largest wholesale house in London dealing in white lead, whose connections and trade relations embrace literally the whole world, we have learned that not 1000th part of the *lead*, as it is technically termed, of good and saleable quality met with in the trade, is made by these new processes, since the products of most of them are deficient in some respect or other.

Theory of Preparing White Lead.—Leaving out of the question the preparation of white lead from lead sulphate, the preparation of the pigment as regards all the other methods is dependent upon:—

1. The formation of basic lead acetate;

2. The decomposition of that compound into neutral lead acetate and white lead. Viewing white lead for this purpose simply as a lead carbonate, although we shall presently see that the white lead of commerce is not so simply constituted, the formation may be illustrated by the following formulæ:—

$$\text{I.}\quad \underbrace{2\left\{\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O}_{\text{Acetic acid.}} + 3PbO = \underbrace{\left\{\begin{matrix}(C_2H_3O)_2\\Pb\end{matrix}\right\}O_2, 2PbH_2O_2}_{\text{Basic lead acetate.}};$$

$$\text{II.}\quad \underbrace{\left\{\begin{matrix}(C_2H_3O)_2\\Pb\end{matrix}\right\}O_2, 2PbH_2}_{\text{Basic lead acetate.}}O_2 + 2CO_2 + \underbrace{2PbCO_3}_{\text{Lead carbonate.}} + \underbrace{\left\{\begin{matrix}(C_2H_3O)_2\\Pb\end{matrix}\right\}O_2}_{\text{Neutral lead acetate.}}.$$

It is therefore evident that a comparatively very small quantity of lead acetate can produce a large quantity of white lead, and the manufacture of that material would be endless but for the fact that white lead retains some neutral lead acetate, and that the loss of acetic acid cannot be practically avoided.

Properties of White Lead.—When unadulterated and well-made, white lead is an exquisitely fine white coloured powder, devoid of taste and smell. The white lead of commerce exhibits, according to the mode of preparation, different features; one preparation is met with in flakes, having been obtained by the corrosion of thin strips of lead placed in pots. The lead known as Krems lead is pure white lead made up into cakes by means of gum-water.

The variety of white lead known as pearl white is blued with either a small quantity of indigo or Berlin blue. The white lead of commerce has frequently been made the object of chemical analysis, especially by Dr. G. J. Mulder and M. Grüneberg. The results of the analyses of the undermentioned samples prove the correctness of the formula given above. The numbers refer to:—1. Krems white lead. 2. Precipitated by the Clichy method and manufactured at Magdeburg. 3. From the Harz. 4. Another sample from Krems. 5. A sample from a chemical laboratory by imitating the Dutch method on a limited scale. 6, 7. Samples from Klagenfurt, Carynthia. . English lead manufactured according to the Dutch method.

	1.	2.	3.	4.	5.	6.	7.	8.
Oxide of lead .	83·77	85·93	86·40	86·25	84·42	86·72	86·5	86·51
Carbonic acid .	15·06	11·89	11·53	11·37	14·45	11·28	11·3	11·26
Water . .	1·01	2·01	2·13	2·21	1·36	2·00	2·2	2·23

It is certain that the covering properties of white lead are dependent upon its state of aggregation, because a loose crystalline white lead does not cover nearly as well as the perfectly amorphous lead prepared by the old Dutch method. It appears that the covering power increases with the amount of hydrated lead oxide. This is proved by the fact that those who merely choose white lead by its covering power are often misled, a fact lately tested by the editor of this work, by giving to a workman, thoroughly acquainted with white lead as commercially met with, a mixture of carefully prepared and dried hydrated lead oxide, to which white precipitate, bismuth subnitrate, and bismuth carbonate had been added. The man, after testing a series of samples of purposely adulterated white lead, all of which he detected as adulterated, was unable to speak with certainty of the above mixture, which he took for pure lead.

Adulteration of White Lead.—It has been, and is still, to some extent, the custom in manufactories to add to white lead a certain quantity of barium sulphate either native or artificially prepared. Lead is often mixed with lead sulphate, chalk, barium carbonate, barium sulphate, and pipe-clay; but these adulterations are most common in the retail trade. None of these substances ought to be present; they possess no covering power and needlessly absorb oil. Pure white lead ought to be perfectly soluble in very dilute nitric acid, and in the resulting clear solution caustic potassa should not produce a precipitate. A residue insoluble in the dilute nitric acid indicates the presence of gypsum, heavy-spar, or lead

sulphate. The lead sulphate may be recognised by reducing the lead with the blowpipe. Barium sulphate can be made evident by ignition with charcoal in the blowpipe flame, treating the residue with dilute hydrochloric acid, and adding a solution of gypsum, which again yields a precipitate of barium sulphate. Gypsum does not yield an insoluble precipitate with dilute nitric acid, but does so with a solution of ammonium oxalate. According to Dr. Stein, the most simple method of estimating quantitatively a mixture of white lead and barium sulphate, is to heat the weighed sample in a piece of combustion-tube, and to collect the carbonic acid in a Liebig's potassa-bulb, a chloride of calcium-tube being fastened by a perforated cork to the combustion-tube to absorb the moisture. The quantity of carbonic acid given off stands in direct proportion to the quantity of lead carbonate present. Pure white lead of good quality gives off about 14·5 per cent. of the gas, and, according to Dr. Stein's researches, the undermentioned series of mixtures gave off the quantities of carbonic acid indicated :—

33·3	parts of white lead	and	66·6	parts of heavy-spar	lost by ignition	4·5–5	per cent.	
66·6	,,	,,	33·3	,,	,,	,,	6·5–7	,,
80·0	,,	,,	20·0	,,	,,	,,	13·0	,,
50·0	,,	,,	50·0	,,	,,	,,	10–10·4	,,

Applications of White Lead.—The extensive applications of this material as a constituent of paints, "to give body," as the term runs, and as putty, and for various chemical operations are well known. It has been experimentally proved by Dr. G. J. Mulder in his treatise *On the Chemistry of Drying Oils and the Practical Applications to be drawn therefrom*, that the quantity of white lead used in proportion to linseed oil for painting purposes is far too great, being on an average from 250 to 280 parts of white lead to 100 parts of oil, while the author found that 52 parts of unadulterated white lead, or 44 parts of oxide of lead (PbO) to 100 parts of raw or boiled linseed oil are amply sufficient quantities. White lead, however useful, is very sensitive to the action of sulphuretted hydrogen, by which it is blackened and discoloured, causing not only all the white paint to be spoiled, but also all pigments and paints of which white lead is a constituent, as may be seen to a very large extent every summer at Amsterdam, where sulphuretted hydrogen is abundantly given off from the stagnant canals. The action, however, of the sea air in autumn has the effect of somewhat restoring the blackened and discoloured painted surfaces to their primitive hue. Thénard suggested that pictures which had become blackened should be cleaned by means of hydrogen peroxide, the oxygen of which present as ozone converts the blackened lead colours into white lead sulphate.

In this country it has become an almost universal custom to sell white lead ready ground with linseed oil into a thick paste. This practice certainly saves painters a great deal of trouble, but is also pregnant with the difficulty of detecting adulteration, while there is a chance of an inferior oil, rosin oil, being added. The oil almost entirely prevents the action of any acid upon the paste; even if very strong nitric acid be taken, and heat applied, the decomposition and disintegration are very slow and incomplete, and, besides, owing to the insolubility of lead nitrate in nitric acid, the action of strong nitric acid upon oil thus mixed gives rise to a variety of compounds, which interfere with the usual modes of testing the white lead. To remove the oil in order to test white lead, the best plan is to thoroughly incorporate some of the sample with a mixture of chloroform and strong alcohol in equal parts, and to wash the mass by decantation or on a filter with a fluid composed of 2 parts of chloroform and 1 of strong alcohol. The quantity of the oil may then be ascertained by the evaporation of this solvent. After washing once or twice with boiling

alcohol and then drying, the white lead can be readily tested by any of the known methods.

The proposed electrolytic method of producing white lead seems not to promise good results.

White Lead from Chloride of Lead.—M. Tourmentin prepares white lead from basic lead chloride, obtained by the action of common salt upon litharge, by mixing that compound with water, passing through it a current of carbonic acid, and next boiling the fluid in a leaden-pan with powdered chalk until a test sample, when filtered, does not become blackened by the addition of ammonium sulphide. The white lead thus formed is freed from salt by washing with water.

Basic Lead Chloride as a Substitute for White Lead.—Mr. Pattinson, of the Felling Chemical Works, near Newcastle-on-Tyne, has proposed that, instead of white lead, a basic lead chloride (oxychloride) should be used, and he prepares that substance by adding to a hot solution of lead chloride ($PbCl_2$), containing from 400 to 500 grammes of the salt to the cubic foot, an equal bulk of saturated lime-water. This addition causes the throwing down of the compound ($PbCl_2 + PbH_2O_2$), which, after having been collected on a filter and washed, is dried and used as a pigment. The lead chloride is obtained directly from galena, which is decomposed in leaden vessels with strong hydrochloric acid. The sulphuretted hydrogen thus formed is carried by suitable tubing to a burner in the sulphuric acid chamber, the resulting sulphurous acid from the combustion being used for the production of sulphuric acid. Pattinson's white lead is not so white as ordinary white lead, its colour verging to yellow, but this is no objection where white lead is to be used with other paints, and the less so as Pattinson's oxychloride of lead covers well.

Lead Sulphate ($PbSO_4$), obtained as a bye-product in the preparation of aluminium acetate from alum and sugar of lead, or in obtaining acetic acid by the action of sulphuric acid upon lead acetate, or in a very impure state as a deposit in the lead chambers of sulphuric acid works, is a difficult bye-product to utilise. It cannot be easily reduced to metallic lead, and its low covering power prevents its use as a pigment. It may be used in the manufacture of lead chromate (which see).

Cassel Yellow and Turner's Yellow.—If 1 part of ammonium chloride is melted with 10 parts lead oxide there is produced a yellow foliaceous crystalline mass, which, when finely ground and elutriated, is sold as Cassel yellow. Its composition is said to be $PbCl_2,7PbO$. If lead oxide is treated with solution of sodium chloride, a white lead oxychloride is produced, which, after melting, is known as Turner's yellow. Its formula is $PbCl_2,5PbO$. Both these preparations have been superseded by chrome yellow.

COMPOUNDS OF MANGANESE AND CHROMIUM.

Manganese.—Of all the ores of manganese met with in various degrees of oxidation, only the peroxide, mineralogically known as pyrolusite, polianite, and technically as glass-makers' soap, is industrially of much importance. When perfectly pure this mineral consists of 63·64 per cent. of manganese, and 36·36 per cent. of oxygen, its formula being MnO_2; but the ore, as met with in commerce, frequently contains baryta, silica, and water, and sometimes oxides of iron, nickel, cobalt, and lower oxides of manganese—viz., Braunite, Mn_2O_3; Manganite, Mn_2O_3,H_2O; Hausmannite, Mn_3O_4; and various other minerals, as potassa compounds, lime, &c. In Germany the ore is purified by most ingeniously contrived machinery, which might be very advantageously applied to a great many other metallic ores and phosphatic minerals. Manganese is industrially employed in making oxygen, the preparation of bromine and iodine, glass-making, colouring enamels, for producing mottled soaps, in puddling iron, and in dyeing and calico-printing, for preparing potassium permanganate; but the largest

consumers are the manufacturers of chlorine. The bulk of the manganese of commerce is derived from Germany, which supplies about 700,000 cwts. to Europe annually. It is found also very largely and of excellent quality in Spain, as well as in Italy, Greece, Turkey, Sweden, and British India.

Testing the Quality of Manganese.—The value of manganese for technical purposes depends—1. On the quantity of oxygen it is capable of yielding, or the quantity of chlorine it will evolve, not taking into account the O of the MnO. 2. On the nature and quantity of the substances soluble in acids, such as the calcium and barium carbonates and ferrous oxide, which, not yielding chlorine, saturate a certain quantity of hydrochloric acid. But even if these impurities are absent, it may happen that, of two samples of manganese, one requires more acid than the other to evolve the same bulk of chlorine gas, as, for instance, when one of the samples contains in addition to manganese peroxide (MnO_2) also the sesquioxide (Mn_2O_3), especially if the latter is present as hydrate. 3. On the quantity of water, which may amount even to 15 per cent.

According to the experiments of Fresenius, the most suitable temperature for drying a weighed sample of manganese, in order to estimate the water it contains, is 120°, no water of hydratation being expelled at that heat; but for commercial analysis the drying of a sample at 100° is quite sufficient, provided it be kept at that heat for some hours consecutively. Among the many methods proposed for testing manganese, that originally invented by Thompson and Berthier, and improved upon by Will and Fresenius, is based on the fact that a molecule of manganese peroxide treated with sulphuric acid is capable of converting, by the O given off, 1 mol. of oxalic acid into 2 mols. of CO_2.

From the weight of CO_2 evolved the quantity of manganese peroxide actually present in the sample is calculated.*

Potassium Permanganate.—This salt ($KMnO_4$), used for disinfecting, bleaching, and other oxidising purposes, and constantly employed in chemical laboratories, owes its efficiency to the fact that, in contact with dilute sulphuric acid, it yields manganous oxide and oxygen ($Mn_2O_7 = 2MnO + 5O$). The potassium permanganate is for technical purposes prepared in the following manner:—500 kilos. of caustic potassa solution at 84° Tw. (= 1·44 sp. gr.) are added to 105 kilos. of potassium chlorate, and the mixture evaporated to dryness, there being gradually added 180 kilos. of powdered manganese, and the heating continued to the fusion of the mass, which is stirred until cold. The powder thus obtained is heated in small iron crucibles to a red heat, and when semi-fluid is cooled; the mass is next broken up and put into a large cauldron filled with hot water, and left standing for about an hour. The clear liquid having been decanted from the sediment, hydrated manganese peroxide, is evaporated to crystallisation; 180 kilos. of manganese yield 98 to 100 kilos. of crystallised permanganate. Approximately the process may be elucidated as follows:—

(*a*) By the fusion of the potassium manganate and potassium chloride—

$$6MnO_3 + 2KClO_3 + 12KOH = 6K_2MnO_4 + 2KCl + 6H_2O.$$

(*b*) During the solution of the fused mass in water, the potassium manganate is converted into potassium hydrate, hydrated manganese peroxide, and potassium permanganate, $3K_2MnO_4 + 6H_2O = 4KOH + 2KMnO_4 + MnO_2 + 4H_2O$. Consequently one-third of the manganic acid is lost by the formation of manganese peroxide. This also occurs when, according to M. Tessié du Motay's plan, the conversion of potassium manganate into permanganic acid is effected by magnesium sulphate—$3K_2MnO_4 + 2MgSO_4 = 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2MgO$. Dr. Staedeler therefore suggests that the potassium manganate should be converted into permanganate by chlorine, according to the formula—$2K_2MnO_4 + Cl = KCl_2 + 2KMnO_4$. For disinfecting

* See *Select Methods in Chemical Analysis*, by W. Crookes, F.R.S.

purposes a mixed sodium and potassium permanganate, or even the latter alone, is usual; the well-known Condy's fluid is a solution of this salt in water. Kuhne's disinfectant is a mixture of sodium permanganate and ferric sulphate. Potassium permanganate is used to some extent in dyeing, and for staining wood.*

The Berlin Joint-Stock Chemical Company produces permanganates by the electrolysis of a manganate.

Chromates.—The yellow, neutral salt, K_2CrO_4, is prepared by heating chrome iron ore, previously pulverised and elutriated, with potassium carbonate and nitrate on the hearth of a reverberatory furnace. The oxygen of the saltpetre causes the higher oxidation of the ferrous oxide and chromium sesquioxide, the latter being converted into chromic acid. The thoroughly sintered, not molten, mass is, after cooling, again ground up and lixiviated with boiling water, and also boiled for a time to extract the neutral potassium chromate. Wood vinegar is added to the solution to precipitate the alumina and silica, after which the clear liquid is evaporated, until a film of saline material begins to form, when it is left to crystallise. The crystals take a column-like form, and are of a lemon-yellow colour, readily soluble in water, but insoluble in alcohol, and having a great tendency to become converted into potassium bichromate or red chromate. This conversion of the neutral salt into the bi- or acid- salt is at once effected by the addition to its solution of sulphuric or nitric acid—preferably the latter, on account of the formation of potassium nitrate, which may be either sold or used in the manufacture of the neutral chromate.

The potassium dichromate or acid chromate, $K_2Cr_2O_7$, crystallises in anhydrous, aurora-red coloured triclinohedric prismatic crystals, soluble in 10 parts of water. This solution is highly caustic and poisonous. When heated to redness the salt gives off oxygen, leaving chromium oxide and neutral potassium chromate in the retort.

Jacquelain proposes that the chrome-iron should be mixed with chalk and the mixture heated and frequently stirred, then cooled, pulverised, and put into water, with the addition of enough sulphuric acid to produce a weak reaction, the result being the formation, first of calcium chromate, which, by the addition of the acid, becomes the bichromate of that base. The ferrous sulphate present in this solution is precipitated by means of chalk. In order to convert the calcium bichromate into the corresponding potassium salt, it is only necessary to add a solution of potassium carbonate, the result being of course the precipitation of calcium carbonate and the exchange of the chromic acid from the lime to the potassa. According to Tilghman's process chrome-iron ore is mixed with 2 parts of lime, 2 of potassium sulphate and heated for eighteen to twenty hours in a reverberatory furnace. The same inventor suggests the heating of chrome-iron ore with powdered felspar and lime. Mr. Swindells ignites chrome ore with equal parts of either sodium or potassium chloride to the highest possible white heat, at the same time exposing the mixture to a constant current of superheated steam, the formation of sodium or potassium chromate resulting. The most important improvement in the preparation of potassium chromate is the substitution of potash for saltpetre and the use of a furnace so constructed as to admit of the proper access of air to the strongly heated mass, the oxygen of the air being made to oxidise the chromic oxide to chromic acid. Another improvement is, that in using lime instead of alkali, the oxidation of the chromic oxide is greatly accelerated, by reason that when lime is employed instead of potassa the heated materials do not become semi-fused or pasty, but, remaining pulverulent, admit of the readier access of air, as well as preventing the sinking, on account of higher specific gravity, of a portion of the chrome ore to the bottom of the hearth, and there becoming withdrawn from the action of the heat.

* Latterly sodium permanganate has been prepared and used at great expense for deodorising the Thames.

Applications of the Potassium Chromates.—Before the year 1820 the salts spoken of were only used for the preparation of chrome-yellow; their preparation was then very expensive, viz., the calcination of the chrome-iron ore with potassium nitrate only. At this date M. Kœchlin discovered the applicability of potassium dichromate to the obtaining of what is technically termed "discharge" for Turkey red—a madder colour—a discovery soon followed by others bearing upon the useful applications of this salt, among which are the formation of chrome-yellow and chrome-orange in calico-printing, chrome-black in dyeing, the oxidation of catechu and Berlin blue, the discharge of indigo blue, the bleaching of palm oil and other fatty substances, the preparation of mixtures for the heads of lucifer matches, the preparation of mercurous chromate and chromic oxide as green-coloured pigments in glass- and china-painting, and for the preparation of Guignet's Green, a peculiar hydrated chromium oxide, $Cr_2O_3 2H_2O$, obtained by heating 1 part of potassium bichromate and 3 parts of crystallised boric acid, and used as a pigment in calico-printing. As might be expected, all these discoveries gave a strong impulse to the manufacture of the potassium chromates, which have recently found still further useful applications in the obtaining of colours from coal-tar—*i.e.*, aniline violet, aniline green, and alizarine, in the manufacture of chlorine gas, in defuseling brandy and other spirits, and in the purification of wood-vinegar made from the crude pyroligneous acid.

According to M. J. Persoz, there exist, America excepted, only six manufactories of the potassium chromates—viz., two in Scotland, one in France, one at Trjöndhem, Norway, and one at Kazan, near the Oural, Russia; the total production of these works amounted in 1869 to 60,000 cwts.*

Sodium Chromate (Na_2CrO_4).—Walberg mixes 6 parts finely-ground chrome ore (containing 44 per cent. Cr_2O_3), 3 parts soda-ash (containing 92 per cent. sodium carbonate), and 3 parts chalk in a reverberatory in the oxidising flame; the charge of the furnace being 1 ton. The hot mass is lixiviated with water, forming a lye of 84° Tw. It is then boiled down in an iron pan to 104° Tw., and poured into tanks lined with lead. When cold, there are formed acicular yellow crystals of

$$Na_2CrO_4.10H_2O.$$

They are drained in a centrifugal machine, placed in a drying-chamber, at a heat not exceeding 30°, and well ventilated. Here they effloresce, and are converted into a yellow anhydrous powder.

Sodium chromate so prepared has the composition—

Na_2CrO_4	96·60
Sodium sulphate	0·92
Insoluble residue	0·40
Water	1·28
	99·20.

For producing sodium dichromate, Chrystal ignites chrome ore with lime and soda, lixiviates, decomposes the neutral chromate with an acid, and evaporates to crystallisation. Ammonium chromates may be obtained from the sodium salts by double decomposition.

Chromic Acid, CrO_3, is obtained by decomposing potassium dichromate with sulphuric acid. It is used in galvanic batteries in place of nitric acid.

Chrome-Yellow, Lead Chromate ($PbCrO_4$), is not to be confounded with *yellow chrome*, the neutral potassium chromate. There are in technical use three different compounds of lead and chromic acid—viz., neutral lead chromate or chrome-yellow, basic chromate or chrome-red, and a mixture of these two salts constituting chrome-orange. The first of these substances is obtained by two methods:—(1) By the

* There is also a manufactory of the chromates at Sowerby Bridge, near Halifax.

precipitation of a solution of potassium chromate with a solution of lead acetate; or (2) by the use of lead sulphate or chloride. According to the first plan, the operation begins with the preparation of a solution of lead, for which purpose granulated lead is put into wooden tubs placed one above the other, and the taps each tub is provided with being turned off, vinegar is poured into the upper tub. In about ten minutes the tap at the bottom of the tub is opened, and the contents let into the second tub. The operation is repeated with all the tubs, four to eight in number, the object simply being to moisten the lead thoroughly with the vinegar, so as to cause rapid oxidation on its subsequent exposure to air. The metal soon becomes coated with a bluish-white coloured film, and when this is apparent, vinegar is again poured into the topmost tub and left for about an hour, after which it is run off into the second tub, and the operation continued until there is obtained a saturated solution of basic lead acetate. To prepare chrome-yellow enough vinegar is added to obtain an acid reaction, and the fluid left to deposit any suspended sediment. At the same time, in another tub, a solution of 25 kilos. of potassium bichromate in 500 litres of water is kept in readiness. The clear lead solution is next poured into the bichromate solution as long as any precipitate ensues. This precipitate is well washed, and usually mixed with gypsum, or barium sulphate, to obtain the lighter chrome colours; finally it is dried. According to Liebig, chrome-yellow is obtained from lead sulphate, an almost useless bye-product from calico-printing and dye-works, by digesting it with a warm solution of neutral potassium chromate. The depth of colour of the ensuing yellow pigment depends upon the quantity of lead sulphate which is converted into lead chromate. The white lead deposit from the sulphuric acid chambers is too impure for this use.

Dr. Habich states that there exist two binary compounds of lead chromate and sulphate, the formulæ of which are:—$PbSO_4 + PbCrO_4$ and $2PbSO_4 + PbCrO_4$. The former is obtained when a solution of potassium bichromate, previously mixed with enough sulphuric acid to cause its dissociation, is precipitated with a solution of lead; while the second compound is formed if the quantity of sulphuric acid is doubled. When dry it has a bright, sulphur-yellow colour with a fiery fracture. According to M. Anthon a beautiful chrome-yellow is obtained by the digestion of 100 parts of freshly precipitated lead chloride with 47 parts of potassium bichromate.

Chrome-Red.—The basic lead chromate, known as chrome-red and Austrian cinnabar, $PbCrO_4 + PbH_2O_2$,* is a red-coloured pigment much in demand, and obtained from the yellow or neutral lead chromate, either by boiling it with a caustic potassa solution, or by fusing it with potassium nitrate, the effect being that half of the chromic acid is withdrawn from the neutral chromate. Liebig and Wöhler state that chrome-red is best obtained by fusing together, at a very low red-heat, equal parts of potassium and sodium nitrates, gradually pouring into the fused salt small quantities of chemically pure yellow lead chromate. After cooling, the insoluble chrome-red is well washed and dried. It is then a magnificently coloured cinnabar-like crystalline powder. Dulong prepares chrome-red by precipitating a solution of lead acetate with a solution of potassium chromate to which caustic potassa has been added. The various shades and qualities of chrome-red, from the deepest vermilion to the palest red, are due to the difference in size of the constituent crystalline particles. This fact is proved by experiment, for when several samples are uniformly ground to a fine powder the result is the production of a uniformly deep-coloured hue. In preparing chrome-red of a deep colour, everything which might interfere with or injure the crystallisation has to be avoided. The pigments commercially known as the chrome-orange colours are mixtures, in varying proportions, of the basic and neutral

* According to Dr. Duflos (see *Handbuch der Angewandten Pharmaceutisch-Technisch Chemischen Analyse. &c.*, Breslau, 1871, p. 293) the formula of this substance is, $2PbO,CrO_3$, and the dried salt does not contain any water as a component part.

lead chromates, and are usually made by boiling chrome-yellow with milk of lime. M. Anthon recommends for the preparation of a good chrome-orange the treatment of 100 parts of chrome-yellow with 55 parts of potassium chromate and 12 to 18 parts of caustic lime made into milk of lime.

Chromic Oxide or Chrome-Green.—This substance, Cr_2O_3, is used in glass- and porcelain-staining as a *couleur grand feu*, that is to say, it stands the most intense heat, provided no reducing materials are allowed to affect it. It is commercially known under the name of chrome-green as an indelible pigment for printing, being especially employed for bank-notes. It is prepared in various ways, the finest being obtained by heating mercurous chromate, but this method is far too expensive to admit of any extensive application. Lassaigne heats equal molecules of sulphur and yellow potassium chromate, and exhausts the mixture with water, leaving the insoluble green sesquioxide behind. Wöhler prefers to mix the yellow potassium chromate with sal-ammoniac, to heat that mixture, and afterwards treat it with water, leaving the insoluble chrome-green as a fine powder.

Among other methods of preparing the anhydrous sesquioxide is the heating of an intimate mixture of potassium bichromate and charcoal. The hydrated chromium oxide, according to the formula $Cr_4H_6O_9$, is met with in the trade under a variety of names, and often contains boric or phosphoric acids, not, however, as an essential constituent (see Schützenberger's formula for Guignet's green), but as a remnant of imperfect preparation. This hydrated oxide, the preparation of which so as to ensure a good colour is rather a difficult matter, requiring very careful manipulation, is known as emerald green, Pannetier green, Matthieu-Plessy green, and Arnaudon green. The pigment is used as an artist's colour and in calico-printing as a substitute for Schweinfurt green, but is very expensive.

Guignet's green is best obtained by melting together potassium dichromate and crystalline boric acid at a red heat. The melted mass is lixiviated with hot water, and the residue finely ground.

In an English manufactory 8 parts of boric acid and 3 parts potassium dichromate are finely pulverised, well mixed, and heated for four hours to dull redness in a reverberatory. The burnt mass must have a peculiar green tone, which can be recognised only by long experience. In any case the mass must have no (or but few) yellow or brown rusty spots; if these are abundant the entire melt is worthless. Such spots may arise from different causes, the most common of which is a dirty furnace, or too high a temperature. The mass, a mixture of calcium borate and chromic oxide, is washed to remove the former. The waters from the two first washings are kept apart for the recovery of the boric acid. The third is kept to be used for the first washing of a fresh melt, and the further waters are allowed to collect in a cistern, where they deposit any oxide which may have been carried over. The washing lasts six days. The mass is then ground in a wet mill, and washed again, being mixed up with water, and boiled four or five times in the course of the day, each time with fresh water. Heat is applied by blowing in steam. The mass is pressed, yielding a product which, at 100°, contains 33 per cent. of solid matter, and after ignition 26 per cent.

Chromic Hydrate, either alone, or in combination with boric, phosphoric, or arsenic acid, is a fine green pigment, used under the names of Mittler green, emerald green, Pannetier green, Arnaudon green, Schnitz green, and Matthieu-Plessy green.* It is prepared, according to Köthe, by treating 10 grammes potassium dichromate with a solution of 12 grammes sugar in 100 c.c. of water, adding 30 c.c. phosphoric acid of sp. gr. 1·3, and the solution of 10 grammes barium chloride, and boiling for some time.

Dingler's Green is a mixture of chromium and calcium phosphates.

* There is lamentable confusion in the momenclature of pigments.

Casali Green is obtained by igniting 1 part potassium dichromate and 3 parts gypsum and boiling the mass in very dilute hydrochloric acid.

Chrome Alum.—This salt, $\left.\begin{matrix}Cr_2\\K_2\end{matrix}\right\}4SO_4 + 24H_2O$, is obtained in rather large quantities as a bye-product of the manufacture of aniline-violet, aniline-green, and anthracene-red. It is a deep violet-coloured octahedrically crystallised substance, now used to some extent as a mordant in dyeing, for rendering gum and glue insoluble, for water-proofing woollen fabrics, and for the preparation of potassium chromate.

Chromium Chloride.—This compound, Cr_2Cl_6, best prepared by the decomposition of chromium sulphide by means of chlorine, constitutes a crystalline violet-coloured mica-like material, employed in the manufacture of coloured paper and paper-hangings.

Basic Ferric Chromate, $Fe_2(Cr\,O_4)_3$, has been recommended by Kletzinsky by the name of *siderine yellow* as a water- and oil-colour, drying very quickly. It is obtained by heating a solution of potassium dichromate mixed with neutral ferric chloride. It forms a fiery red precipitate, which is carefully washed and dried.

IRON COMPOUNDS, INCLUDING FERROCYANOGEN.

Copperas or Green Vitriol.—The substance called copperas and green vitriol, ferrous sulphate ($FeSO_4 + 7H_2O$), is met with in trade in the form of greenish-coloured crystals possessed of an inky astringent taste; on exposure to dry air the crystals effloresce, and are gradually converted into a yellowish powder—basic ferric sulphate. 100 parts of the chemically pure crystallised salt consist of—

26·10 parts of ferrous oxide.
29·90 „ sulphuric acid.
44·00 „ water.

Preparation of Green Vitriol as a Bye-product in Alum Works.—Since the minerals ordinarily used in the manufacture of alum—the alum schists—generally contain iron pyrites (FeS_2), either as such or already partly converted into a basic sulphate of the peroxide (which on being treated along with the alum shale, becomes by weathering and roasting converted into iron protosulphate and peroxide), green vitriol is frequently a bye-product of alum manufacture, and is obtained by evaporating the mother liquor containing iron, and leaving it to crystallise. In some localities, as, for instance, at Goslar (Prussia), on the Hartz mountains, the liquor obtained by the lixiviation of the iron-containing minerals alluded to is first evaporated for the separation of the green vitriol, then a potassium or ammonium salt is added to the remaining acid liquid to obtain alum.

Preparation of Green Vitriol in Beds.—The material sometimes rather largely found in coal pits, and called brasses (iron pyrites), is collected and placed in layers over a somewhat excavated surface, which has been rendered impervious to water by puddling with clay, and made to incline slightly in one direction, where water-tight tanks stand, into which scraps of old iron are placed with the view of saturating any free acid; the pyrites, placed on these beds to a thickness varying from 1½ to 3½ or 4 feet, is slowly oxidised by atmospheric agency, and the falling rain carries into the tanks a more or less strong solution of copperas, which, when sufficiently concentrated, is slowly evaporated, some scrap-iron being placed in the evaporating-pans.

Green Vitriol from the Residues of Pyrites Distillation.—In countries where iron pyrites abounds, and fuel and labour are sufficiently cheap to make the distillation of sulphur from pyrites a profitable business, the residues are utilised in green vitriol making, a salt which thus made must, of necessity, contain a good deal of impurity.

Green Vitriol from Metallic Iron and Sulphuric Acid.—The brown sulphuric acid or chamber acid, also such waste sulphuric acid liquids as are obtained in the oil and

petroleum refining, are sometimes used as solvents for scrap-iron for the preparation of green vitriol, which may also be made by boiling the finely pulverised puddling and iron refining slags with sulphuric acid.

Green Vitriol from Spathic Iron Ore.—In localities where spathic iron (ferrous carbonate, $FeCO_3$) occurs in a pure state, that mineral may be usefully applied to the preparation of green vitriol by treatment with sulphuric acid, and evaporating the solution thus obtained. The ferrous sulphate, prepared on the large scale, is often met with crystallised round a small thin stick of wood, which is hung up in the solution to promote crystallisation; sometimes, at least abroad, a so-called black vitriol is met with, which is simply green copperas superficially coloured black by means of some astringent decoction, such as nut galls.

Uses of Green Vitriol.—This substance is employed as a disinfectant, as a mordant in dyeing and calico printing for various black and brown shades, for the preparation of ink, the deoxidation of indigo—in the so-called cold vat used for cotton dyeing—in gas purifying, in the precipitation of gold from its solutions, in the preparation of Prussian blue, in the manufacture of fuming (Nordhausen) sulphuric acid, in the treatment of sewage, and for a host of other purposes.

Iron Minium is a dark red-brown pigment, consisting chiefly of ferric oxide. It is obtained by roasting, sorting, and grinding burnt pyrites.

Potassium Ferrocyanide.—The yellow-coloured salt, generally known as yellow prussiate of potassa (potassium ferrocyanide, $K_4FeCy_6 + 3H_2O$), is, in a technical point of view, a very important substance. It crystallises in large lemon-coloured prismatic crystals, which are not affected by exposure to air, are not poisonous, and possess a sweetish bitter taste. This salt is soluble in 4 parts of cold and 2 of boiling water, but is insoluble in alcohol; in 100 parts there are—

37·03	Potassium	
17·04	Carbon	} Cyanogen.
19·89	Nitrogen	
13·25	Iron	
12·79	Water	

At 100° the water is driven off. The salt is prepared on a large scale by igniting such carbon as contains nitrogen to a red heat with potassium carbonate in closed vessels. The quantities of the materials may be varied, the relative proportions being given by some makers as 100 parts of potassium carbonate to 75 of the nitrogenous carbon, or, according to Runge, 100 parts of potassium carbonate, 400 of torrified horn, and 10 parts of iron filings. The nitrogenous materials used are horns, hoofs, blood, wool-dust, cuttings of hides, and leather.

The fusion of these ingredients is carried on either in closed iron vessels of a

Fig. 374.

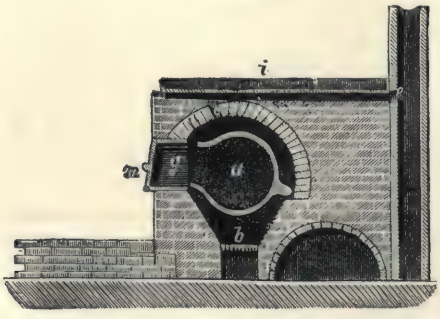
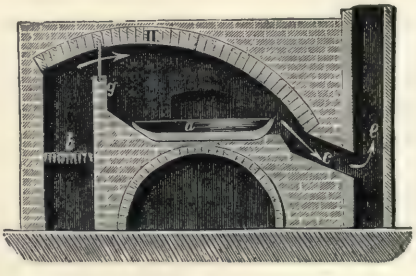


Fig. 375.



peculiar shape, or in a reverberatory furnace. The iron-vessel, *a*, termed a muffle, (Fig. 374), is egg- or pear-shaped, having a diameter of 1·2 metre, a width of 0·8 metre,

and varying from 12 to 15 centimetres in thickness, with a short, wide neck in front. As shown in the woodcut, the iron vessel is placed in the furnace in such a manner as to be exposed to the action of the flame and hot gases on all sides, being supported at the back by a projection about 27 centimetres long, and resting at *g* on the brick-work, leaving space sufficient for the gases generated in the interior to pass off by *c* into the chimney-flues; *m* is an iron cover which is closed during the operation of melting, *g* being an opening in the front wall of the furnace, through which the ingredients are put into the iron vessel, and the molten mass taken out. The shallow pan, *i*, on the top of the furnace, is intended for the evaporation of the liquor obtained by treating the molten mass with water. The use of the iron vessel, however, is attended with the serious drawback that the iron is eaten into holes in a comparatively short space of time; and, though this action is greatest on the lower part of the vessel, and it may therefore be turned bottom upwards, and the holes stopped with fire-clay, the vessel has soon to be replaced by another. It is on this account, and also owing to the fact that a larger quantity of raw material can be operated upon at once, that instead of the apparatus described above, there has come into general use a reverberatory furnace, Fig. 375, arranged with a shallow cast-iron pan, *a*, from 1 to 1·8 metre in diameter, with a rim about 1 decimetre high; *b* is the fire-place; *g*, the bridge; *c*, a flue leading to the chimney, *e*. Sometimes the hot air is applied to the heating of evaporating pans, being carried under them before entering the chimney. The result of the ignition is the formation of a black mass, technically called *the metal*, yielding the liquor from which the crude salt crystallises. The salt is purified by re-crystallisation, while the black residue is employed as a manure and for decolorising paraffine, &c.

The theory of the formation of the potassium ferrocyanide is as follows:—The carbonate and potassium sulphate, the nitrogenous coal and the iron reacting upon each other, give rise to the formation first of potassium sulphide, which in its turn converts the iron into sulphide, while the nitrogen contained in the charcoal unites, under the influence of potassium, with the cyanogen of the carbon, which again in its turn combines with the potassium, giving rise to the formation of potassium cyanide. When the fused mass is treated with water, potassium cyanide and sulphide of iron decompose each other, the result being the formation of potassium ferrocyanide and sulphide, the last-named salt remaining in the mother liquor. M. E. Meyer states (1868) that it is more advantageous to employ, instead of the iron sulphide, the carbonate of that metal, for the purpose of converting cyanogen into ferrocyanogen, because the potassium ferrocyanide crystallises far more completely and freely from solutions not containing any potassium sulphide. Liebig has since proved that the fused mass only contains potassium cyanide and metallic iron, and not any potassium ferrocyanide, which is only formed by treating the molten mass with water, or more slowly by its exposure to moist air. Among the materials frequently added to the fusing mass are—scraps of metal, the refuse of leather, dried blood and other dry animal offal, because the ammonia evolved by their decomposition in the presence of an alkali aids the formation of potassium cyanide. According to M. P. Havrez, the crude suint obtained from wool is an excellent material for the preparation of potassium ferrocyanide, since 100 kilos. of the suint contain about 40 kilos. of potassium carbonate, from 1 to 2 kilos. of potassium cyanide, and about 50 kilos. of combustible hydrocarbons, the heating value of which is at least equal to that of 40 kilos. of coal.

Attempts have been made to obtain the potassium cyanide on a large scale, by causing a current of ammoniacal gas to pass through and over potassium carbonate heated to redness; and also to obtain potassium cyanide from, or by aid of, the nitrogen of the atmosphere. This process was tried nearly forty years ago at Bramwell's works near Newcastle-on-Tyne, but was found to be a failure commercially.* As it has

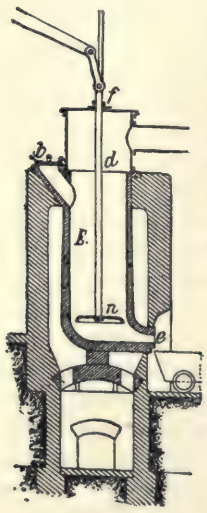
* Compare Richardson and Watts' *Chemical Technology*.

been proved by experiment that baryta, far more readily than potassa, converts carbon and nitrogen into cyanogen, forming barium cyanide at a lower temperature, baryta might perhaps be substituted for potassa, but as yet this plan is not carried out commercially. According to Gélis (1861), the yellow prussiate may be prepared by the mutual reaction of carbon sulphide and ammonium sulphide, the resulting sulphocarbonate being converted into potassium sulphocyanide by means of potassium sulphuret, by which reaction ammonium sulphide and sulphuretted hydrogen are volatilised. The potassium sulphocyanide is next converted into ferrocyanide by being heated with metallic iron to redness, iron sulphide being at the same time formed. It is evident that this process could not be carried out commercially. Mr. H. Fleck described, in 1863, a plan for preparing the ferrocyanide by the action of a mixture of ammonium sulphate, sulphur and carbon, upon fusing potassium sulphide, which thus becomes potassium sulphocyanide, one-half of the nitrogen of the ammonium sulphate remaining in the fused metal as cyanogen, while the other half escapes as ammonium sulphide, which is again converted into ammonium sulphate. The potassium sulphocyanide produced is treated with metallic iron at a red-heat, and thus potassium cyanide and iron sulphide are produced. This process is also too cumbrous and expensive on a large scale.

Applications of the Yellow Prussiate.—This salt is employed in the manufacture of the ferricyanide or red prussiate, in the preparation of Berlin blue, and of potassium cyanide (the impure salt as met with in commerce), in dyeing and calico-printing for the production of blue and brown-red colours, for the purpose of surface-hardening small iron articles, as an ingredient of white gunpowder, and for use in chemical laboratories.

Great loss is experienced in the manufacture of ferrocyanide because the nitrogenous organic matter floats and burns upon the surface of the melting potash, whilst the nitrogenous gases only pass through a thin layer of potash, so that a part escapes without being utilised. To prevent this the potash is melted in the pan *E* (Fig. 376), 2 metres high, and 0·6 metre wide, and the nitrogenous bodies are pressed down to the bottom by a plunger, *n*. This plunger consists of a strong bordered plate of metal with several perforations, its rod, *d*, being raised and lowered by means of a counterpoise. In working, 300 kilos. of potash are melted in the cylinder, the plunger is raised, and the nitrogenous matters are introduced through *b*. The mass is forced to the bottom by lowering the plunger. The introduction of the nitrogenous matter continues until all is melted up. The heat is then raised for a short time; the melt is drawn off at *e* into a truck, and a new charge is introduced. The ammonia in the vapours is condensed in a scrubber.

Fig. 376.



For obtaining ferrocyanide from Laming's mass, Kunheim dissolves out the ammonia with water and the free sulphur with carbon disulphide. It is then mixed with dry lime. The dry mixture is then either heated from 40° to 100° in a closed vessel, with constant stirring to expel any undissolved ammonia, the escaping vapours being passed through a scrubber, and the mass then submitted to methodical lixiviation with water, or the lixiviation is applied first, yielding an ammoniacal lye of calcium ferrocyanide. This lye is carefully neutralised and heated to the boiling point, when a sparingly soluble compound is deposited, calcium-ammonium ferrocyanide. It is treated with lime in closed vessels; the compound is decomposed; the escaping ammonia is secured in the usual manner, and a pure lye of calcium ferrocyanide is obtained. It is utilised as Prussian blue by treatment with

ferrous salts and subsequent evaporation. If potassium ferrocyanide is to be produced, calcium-potassium ferrocyanide is first formed by evaporating and adding so much potassium chloride as is sufficient for forming CaK_2FeCy_6. The double cyanide separates out, is filtered off, washed, and boiled with potassium carbonate, which converts it into potassium ferrocyanide.

Potassium Ferricyanide.—The red prussiate of potassa, properly potassium ferricyanide, or Gmelin's salt, K_3FeCy, is prepared on a large scale and extensively used in dyeing and calico-printing. This salt crystallises in prismatically shaped ruby-red-coloured, anhydrous crystals, which consist in 100 parts of—

35·58 Potassium
21·63 Carbon } Cyanogen
25·54 Nitrogen }
17·29 Iron.

It is prepared by submitting either the solution of the yellow prussiate or that salt in powder to the action of chlorine gas until a sample, when heated, yields no precipitate with a solution of a ferric salt. When the dry and pulverised yellow prussiate is acted upon by chlorine gas, the salt is frequently placed in casks, closed so as only to leave a small outlet, while the vessel can be made, by means of machinery, to turn slowly on its axis, so as to bring all the particles of the salt into contact with the chlorine. Sometimes, again, the pulverised yellow prussiate is placed on trays in a chamber, into the top of which chlorine gas is admitted; when no more chlorine is absorbed the newly formed salt is, if a solution of the yellow prussiate has been operated upon, evaporated to dryness, or in the case where the dry powder of the salt has been taken, the newly formed salt is dissolved in the smallest possible quantity of water, and the solution left to crystallise, the mother liquor containing potassium chloride. This reaction is represented by—

$$\underbrace{K_4FeCy_6}_{\text{Yellow prussiate.}} + Cl = KCl + \underbrace{K_3FeCy_6}_{\text{Red prussiate.}}.$$

The powdered red prussiate is of an orange-yellow colour. According to M. E. Reichardt (1869), bromine may be successfully employed instead of chlorine for the preparation of this salt, which is chiefly used for dyeing woollen fabrics blue, and, with solutions of caustic soda or potassa, for the Mercerising process of cotton.

Potassium Cyanide, KCy.—This salt is obtained in an impure state—Liebig's or crude potassium cyanide—by the fusion of the yellow potassium prussiate in a porcelain crucible, continued as long as nitrogen escapes. Iron carbide sinks to the bottom of the crucible, while the crude cyanide is poured off in a state of fusion—

$$(K_4FeCy_6 = 4KCy + FeC_2 + 2N).$$

According to Liebig's plan, the potassium cyanide is prepared by fusing 1 mol. of potassium ferrocyanide with 1 mol. of potassium carbonate; by this method 10 parts of the ferrocyanide yield 8·8 potassium cyanide, mixed with 2·2 parts potassium cyanate. For all technical and industrial purposes it is far cheaper to use cyan-salt, a mixture of the potassium and sodium cyanides, prepared by fusing together 8 parts of previously dried (anhydrous) potassium ferrocyanide and 2 parts of sodium carbonate. As this mixture fuses readily, the iron carbide easily separates; moreover, the salt thus obtained is less liable to decomposition on exposure to air, and its preparation requires less heat. The industrial applications of the crude potassium cyanide, or of the cyan-salt, are the following:—In the process of electro-gilding, for the preparation of *Grénat soluble*, potassium isopurpurate, from picric acid, and in the reduction of metals. It has been mentioned, while treating of the blast-furnace process, that potassium cyanide is formed during the reduction of iron.

Prussian Blue.—This substance, so named when it was accidentally discovered at

Berlin, in 1710, by Diesbach, is chemically an iron ferrocyanide, more correctly ferrous-ferric cyanide. A distinct variety of this substance is known as Paris blue. Three different kinds of Berlin blue are known, viz., neutral, basic, and a mixture of the two, differing in composition and prepared by different processes.

(*a*) Neutral Berlin blue, also known as Paris blue, is obtained by pouring a solution of yellow prussiate into a solution of iron chloride, or into a solution of a peroxide salt of iron; the result is the formation of a large quantity of a magnificently blue-coloured precipitate, very difficult to wash out, and always retaining a certain quantity of the yellow prussiate, which cannot be removed by washing.

(*b*) Basic Berlin blue is obtained by precipitating a solution of yellow prussiate with a solution of a ferrous salt (green copperas), the result being at first the formation of a white precipitate of ferrous cyanide, which, either by exposure to air, or by the action of oxidising substances, becomes blue; because a portion of the iron is oxidised and another portion takes up the cyanogen thus liberated, converting some of the ferrous cyanide into the corresponding ferric salt, which in its turn combines with the unattacked protocyanide to form Berlin blue, with which, however, some ferric oxide remains mixed. It is stated that basic Berlin blue is distinguished from neutral Berlin blue by being soluble in water; but this solubility is due to the presence of some of the yellow prussiate, and is not a property inherent in the basic Berlin blue in a pure state.

(*c*) As the materials employed on a large scale are neither pure ferrous nor pure ferric salts, but a peroxide containing protosalt of iron, the precipitate obtained consists at first of a mixture of neutral Berlin blue with more or less of the white ferrous cyanide, which afterwards becomes basic Berlin blue; accordingly the Berlin blue of commerce is a variable mixture of neutral and basic Berlin blues. The iron salt employed is green copperas (ferrous salt), which of course should not contain any appreciable amount of copper, the salts of this metal, as is well-known, yielding with yellow ferrocyanide a chocolate-brown coloured precipitate.

Old Method of Preparing Prussian Blue.—Ferrous sulphate and alum are dissolved together in boiling rain- or river-water; the fluid, while yet hot, is decanted from any sediment and forthwith poured into a hot aqueous solution of ferrocyanide, care being taken to stir the mixture, and to add the copperas and alum solution as long as any precipitate is formed. The liquor is run off, and the precipitate washed with fresh water, until all the potassium sulphate is removed; after which the precipitate is drained on filters made of coarse canvas. This having been accomplished, the substance is suspended in water in a boiler, and, while being heated to the boiling-point, nitric acid is added; after a few minutes' boiling, the contents of the boiler are poured into a large wooden tub or cask, and strong sulphuric acid is added. The solution is now allowed to stand for some time, during which the blue colour fully develops. The Berlin blue is then thoroughly washed with water, drained on coarse canvas filters, next dried, pressed, and cut into cakes; finally it is dried in rooms heated to 80°. As Berlin blue, when once quite dry, is reduced to powder with great difficulty, and cannot be brought to the state of fine division as when first precipitated, it is also sent into the market in the state of paste. The alumina derived from the alum is so intimately mixed with the blue that the bulk of the mass is thereby increased without any very perceptible decrease in the intensity of the colour. If the quantity of alumina is very much increased, the colour, of course, becomes much lighter, and this variety of Berlin blue is then known as mineral blue; a name also given to a preparation of copper obtained either from the native hydrated copper carbonate, or artificially prepared by precipitating copper nitrate or chloride by means of lime and chalk.*

* The presence of alumina is essentially an adulteration which may be detected by comparison with a genuine sample and observing how much of any inert white powder may be added to the latter to bring it down to the same shade as the former.

Recent Methods of Preparing Berlin Blue.—Among the improvements made more recently, we may briefly notice the following:—1. The mixing of the solutions of copperas and alum with that of yellow prussiate is effected as above described, but great care is taken to prevent any oxidation of the white precipitate, which is converted into an intense blue by being treated with nitro-hydrochloric acid, the chlorine evolved serving as an oxidising agent. The remaining operations, viz., washing, drying, &c., are performed as in the former methods. 2. Ferric chloride solution is employed for the purpose of converting the white precipitate into blue, while the ferrous chloride thus formed serves at a subsequent operation instead of ferrous sulphate. 3. In some cases manganic chloride (Mn_2Cl_6), is applied; likewise a solution of chromic acid, a mixture of potassium dichromate and sulphuric acid; but it is self-evident that the application of any of these improvements is dependent, as regards success in a commercial point of view, upon local conditions, and upon the possibility of advantageously obtaining the various ingredients.

Turnbull's Blue.—By mixing together a solution of red prussiate and of ferrous sulphate in such proportions as to prevent the entire saturation of the former salt, there is obtained a blue-coloured precipitate, known in commerce as Turnbull's blue, consisting of $Fe_3Fe_2Cy_{12}$, but also containing some chemically combined ferrocyanide.

Berlin Blue as a Bye-Product of the Manufactures of Coal-Gas and Animal Charcoal.—MM. Mallett and Gautier-Bouchard have proved experimentally that Berlin blue may be obtained as a bye-product of coal-gas manufacture from the ammoniacal liquor, from the spent lime of the purifiers, and from Laming's purifying mixture. The spent lime contains, in addition to the calcium and ammonium cyanides, a good deal of free ammonia, mechanically absorbed in the moist lime. Free ammonia is first removed by forcing steam through the lime, and collecting the ammoniacal gas in dilute sulphuric acid. The lime is next washed with water, and the liquor obtained, containing the cyanogen compounds, is employed for the manufacture of Berlin blue. According to M. Krafft's experiments, 1000 kilos. of spent gas-lime yield, when treated as described, from 12 to 15 kilos. of Berlin blue, and from 15 to 20 kilos. of ammonium sulphate. Mr. Phipson states that 1 ton of Newcastle gas-coal yields a quantity of cyanogen which corresponds to from 5 to 8 lbs. of Berlin blue. The manufacture of animal charcoal also yields, if desired, Berlin blue as a bye-product.

Soluble Berlin Blue.—As ordinary Berlin blue is quite insoluble in water, and the basic variety is only soluble in the presence of potassium ferrocyanide, these pigments are only fit for use as paints, and the discovery of the solubility of pure Berlin blue in oxalic acid is of some importance, for thereby its employment as a water-colour becomes possible. This soluble blue is obtained by digesting the Berlin blue of commerce for one to two days, with either strong hydrochloric acid or with strong sulphuric acid, which latter, after having been mixed with the Berlin blue previously pulverised, is diluted with its own bulk of water. The acid is next decanted from the sediment of blue, and the latter thoroughly washed and dried, and then dissolved in oxalic acid, the best proportions being 8 parts of Berlin blue, treated as just mentioned, 1 part of oxalic acid, and 256 of water. According to other directions, Berlin blue readily soluble in water can be obtained—1. By the precipitation of ferrous iodide with yellow potassium prussiate, care being taken to keep the latter in excess. 2. By mixing a solution of ferric chloride in alcoholic ether (*tinctura ferrichlorati ætherea*, Ph. Russ.) with an aqueous solution of ferrocyanide.

Pure Berlin blue is of a very deep blue colour, with a cupreous gloss; it is insoluble in water and alcohol, is decomposed by alkalies, concentrated acids, and by heat. The lighter and more spongy it is, the better is its quality; it is employed as a pigment and in dyeing and calico-printing, but in case of silks and woollens, pigment-printing excepted, it is obtained on the tissues by a circuitous process. The Berlin blue of

commerce is frequently adulterated with alumina, pipe-clay, kaolin, magnesia, heavy-spar, and, according to Pohl, even with starch-paste coloured blue by means of tincture of iodine.

CONSPECTUS OF INORGANIC PIGMENTS.

Whites.

Bismuth white, pearl white, Spanish white (bismuth oxychloride).
China clay, kaolin.
Hamburg white, Dutch white, Venice white, Tyrol white (white lead with heavy-spar).
Lithophan ($BaSO_4 + ZnS$).
Permanent white, new white, mineral white, blanc fixe ($BaSO_4$).
Pattinson's white lead (basic lead chloride).
Satin white (lime, ZnO and a little indigo).
Vienna white, Vienna lime, Bologna lime (prepared chalk).
White lead, Krems white, pearl white, silver white (lead carbonates).
White lead substitute: Antimony oxide.
Zinc carbonate.
Zincolith, Griffith's snow white (zinc sulphide and barium sulphate).
Zinc white, snow white (zinc oxide).

Reds.

Antimonial vermilion.
Bloodstone (Fe_2O_3).
Chrome red, chrome garnet, chrome vermilion, chrome carmine, chrome orange (basic lead chromate).
Colcothar, Paris red, English red, polishing red, iron minium (Fe_2O_3).
Gold purple, Cassius' purple.
Mineral lake, pink colour (glass flux coloured with tin chromate).
Minium, orange minium, Paris red, gold cinnabar, Saturn cinnabar, mineral orange (Pb_3O_4).
Ochre, terra di sienna, Naples red, red bole, ruddle (ferruginous clays).
Realgar (As_2S_2).
Umber (clayey-brown iron ore).
Umber, Colognese (lignite).
Vermilion, cinnabar, Chinese red (HgS).

Yellows.

Cadmium yellow (CdS). Jaune Brillant.
Cassel yellow, Turner's yellow (lead oxychloride).
Chrome yellow, Paris yellow, Leipsic yellow, Hamburg yellow, crown yellow (lead chromate).
Cobalt yellow.
Litharge, massicot.
Mosaic gold (SnS_2).
Naples yellow (lead antimoniate).
Ochre, gold ochre, Chinese yellow, Lemnian earth (clay containing ferric hydrate).
Orpiment (As_2S_3).
Siderine yellow (iron phosphate).
Ultramarine yellow, barium yellow ($BaCrO_4$).
Zinc yellow (zinc chromate).

Greens.

Brunswick green, mountain green (chiefly copper carbonate).
Bremen green (copper hydrate).
Casali green (chromic oxide).
Chrome green, emerald green, Guignet's green, Victoria green (chromic oxide).
Dingler's green (chromium phosphate).
Gentele's green (copper stannate).
Green cinnabar, Naples green (chrome yellow and Prussian blue).
Malachite, copper green, mountain green (copper carbonate).
Mittler green, emerald green, Pannetier's green, Arnaudon's green, Schnitzer green, Matthieu Plessy's green (chiefly chromium hydrate).
Rinmann's green, cobalt green, Saxon green, Gellert's green, Scheele's green, Swedish green (copper arsenite).
Schweinfurt green, Mitis green, Neuwied green, Leipsic green, Vienna green, imperial green, royal green, Bâle green, Kirschberg green (copper aceto-arsenite).
Ultramarine green.
Verdigris (copper acetate).
Zinc green (zinc yellow and Prussian blue).

Blues.

Azurite, mountain blue, copper lazulite.
Bremen blue (copper hydrate).
Berlin blue, Turnbull's blue, Erlangen blue, Hamburg blue, Milori blue.
Cerulean blue (cobaltous-stannic oxide).
Chrome chloride (violet).
Cobalt blue, cobalt ultramarine, Leyden blue (alumina cobaltate).
Egyptian blue (copper glass).
Mineral blue (Prussian blue mixed with clay).
Oil blue, copper indigo (copper sulphide).
Smalts, king's blue (cobalt-glass).
Ultramarine.

THERMO-CHEMISTRY.

Thermo-chemistry, the doctrine of the heat-processes in chemical combinations and decompositions, does not yet by any means suffice to explain all the various transformations and reactions in chemical manufactures. It yields, however, already a basis for the greater or less probability of the practicability of certain chemical reactions, as in general those compounds are most easily produced which originate with the liberation of heat, whilst those which involve the absorption of heat are generally much more difficult to effect. There are, indeed, many exceptions. Thus, in the formation of ammonia in an aqueous solution from 14 kilos. N, 3 kilos. H, and much water :

$$N + H_3 + aq = NH_3.aq$$

20,400 calories (heat-units) are set free, and yet the reaction is so far practically impossible.

Thermo-chemistry is very important for determining the consumption of heat in the chemical arts, as we can can only decide whether it is possible to economise fuel by improvements in a smelting-furnace, a decomposition-pan, or a distilling apparatus, if we first know the actual minimum heat needed in the process in question. If further experience enables us to estimate the size of cooling-surfaces, the quantity of cooling-water, or of ice in obtaining hydrochloric or nitric acid, for regulating certain processes in colour-works, in the fermentation trades, &c., errors are often committed

in this respect, as the plant is often erected too large—and consequently too costly—or, what is generally still worse, much too small. The right proportions of size can only be determined in advance if we know the quantity of heat which must be produced or removed. Many a plant must be altered at a great expense, or even done away with, because it has been carried out on a basis of assumption, not of calculation. Such calculations unfortunately can only be effected in part, as many of the necessary data are still wanting.

As a unit we generally take the quantity of heat needed to raise the unit weight of water from $\rho°$ to 1°. In chemistry there is generally employed as a unit of weight 1 gramme, and the unit of heat is known as a calorie. Berthelot proposes a unit 1000 times greater. Ostwald, in accordance with the proposal of Schuller and Wartha, takes as the unit K, *i.e.*, that quantity of heat which 1 gramme water loses between the boiling-point and the freezing-point. It is 100 times as great as the specific heat of water between 15° and 18°. With regard to the variable specific heat of water, K is 100·6 *cal.* We may generally put 1 *cal.* (Berthelot's) = 10 K = 1000 *cal.* For technical uses it is preferable to use the kilo. as the unit of weight; whether we in addition take the specific heat of water at 0° or at 18° is seldom of moment in the calculations which here come into question, though the latter value is preferable since the determinations are generally effected at 15° to 18°. As, in using the *cal.*, decimal places are almost always reached, and with K very frequently, the different units are best given up, calculating, in round numbers, by the heat-unit as that quantity of heat which raises 1 kilo. of water from 0° to 1° (or from 17° to 18°). As then all the calculations are carried out with kilo.-molecular weights, but with *cal.* for gramme-molecular weights, the numbers in both cases are equal.

According to the general equation of the mechanical theory of heat, $dQ = dU + dW$, in which dQ is the heat which enters or passes out, dU signifying the change in the internal energy, and dW the external work; in considerable changes of space the mechanical work is to be considered. When gas is evolved the pressure of the air i to be overcome. At 760 mm. of the barometer the pressure of the atmosphere upon each square centimetre of surface 76 × 13·6 = 1033·6 grammes, that is, 10,336 kilos. on 1 square metre. As 425 kilogrammetres are the mechanical heat equivalent to the expansion of 1 cubic metre, 10,336 : 425 = 24·3 heat-units. As the kilo.-molecular weight of all gases = 22·3 cubic metres, in the development of 1 kilo.-molecular of a gas at 0°, 22·3 × 24·3 = 542 units of heat are consumed, but at $t°$ 542 $(1 + 0{\cdot}00367\ t)$ heat-units. In the development of oxygen, $2KClO_3 = 2KCl + 2O_3$, there are required (if the oxygen in the apparatus is cooled down to 0°) to overcome the pressure of the atmosphere for the 3 × 32 = 96 kilos., or 3 × 22·3 = 66·9 cubic metres oxygen, 3 × 542 = 1626 heat-units; if the gas escapes at 20°, 1745 heat-units are required.

This heat is of course liberated again if the gases are absorbed, as in the oxidation of Weldon mud, the production of chloride of lime, &c.

In degasifying coals in the generator, there are required to overcome the pressure for each kilo. of coal corresponding to 0·3 cubic metre of gas, if it leaves the generator at 600°, 0·3 × 24·3 × (1 + 0·00367) = 24 heat-units.

In converting coke into carbon monoxide there is also an increase of volume as

$$C_2 + O_2 = 2CO, \text{ and } C + H_2O = CO + H_2.$$

Let us take as an instance the compounds of chlorine. In the combination of 1 kilo. H with 35·5 kilos. Cl, to form 36·5 kilos. HCl, there are liberated, according to Thomsen, 22,000 heat-units; in the formation of solid sodium chloride from 23 kilos. sodium and 35·5 kilos. chlorine gas, 97,700 heat-units; in the formation of sodium hydroxide from 23 kilos. sodium, 1 kilo. hydrogen, and 16 kilos. oxygen, 101,900 heat-units, whilst the reaction $Na_2 + O = Na_2O$ furnishes 80,400 heat-units.

The attempt to decompose sodium chloride by oxygen—

$$2NaCl + O = Na_2O + Cl_2$$
$$-195{,}400 \quad + 80{,}400 \quad = -115{,}000 \text{ heat-units},$$

appears futile from the enormous requirement of heat-units. The decomposition of sodium chloride by watery vapour—

$$NaCl + H_2O = NaOH + HCl$$
$$-97{,}700 - 57{,}000 + 101{,}900 + 22{,}000 = -30{,}800 \text{ heat-units},$$

would require only 30,800 heat-units, but so far it is impracticable.

General attention is now turned to the production of chlorine from magnesium chloride by ignition in a current of air—

$$MgCl_2 + O = MgO + Cl$$
$$-151{,}000 \quad + 144{,}000 \quad = -7000 \text{ heat-units}.$$

But if we assume that there is first formed from the moist magnesium chloride, magnesium hydrate, the formation heat of which = 149,000 heat-units, only 2000 heat-units are required. Pechiney uses oxychloride. As according to André a fused mixture of $MgO + MgCl_2$ gives 15,400 heat-units, but $MgCl_2.6H_2O + MgO - 600$ heat-units, it may be in part understood why Pechiney's mixture in its production must not be heated above 300°.

If hydrochloric acid is to be obtained from magnesium chloride—

$$MgCl_2 + H_2O = MgO + 2HCl$$
$$-151{,}000 - 57{,}000 + 144{,}000 + 44{,}000 = -20{,}000 \text{ heat-units},$$

there are required 20,000 heat-units. Hence this process as regards its demand for heat is less favourable than the production of chlorine, because the formation-heat of watery vapour is greater than that of hydrochloric acid. The case is still more unfavourable if we set out from crystalline magnesium chloride, since in the formation of $MgCl_2.6H_2O$ from $MgCl_2$, 33,000 heat-units are liberated, and must be again supplied during the decomposition. The evolution of hydrochloric acid on heating hydrated magnesium chloride has not hitherto been explained solely on thermo-chemical procedures.

The oxidation of hydrochloric acid by atmospheric oxygen according to Deacon's process seems simple—

$$2HCl + O = H_2O + Cl_2$$
$$-44{,}000 \quad + 57{,}000 = 13{,}000 \text{ heat-units}.$$

If the sides are properly isolated this temperature suffices to keep the clay at the temperature required without any especial heating of the mixture of hydrochloric acid and air. The size of the subsequent cooling-apparatus depends on the composition and the temperature of the gaseous mixture.

That chlorine water readily passes into hydrochloric acid may be understood from its great solution heat in presence of much water—

$$H_2O + Cl_2 = 2HCl.aq + O$$
$$-68{,}400 \quad + 78{,}600 = 10{,}200 \text{ heat-units}.$$

In order to render the demand for heat in the Pechiney decomposition furnace more intelligible, let it be supposed that the composition of the mixture decomposed at 1000° is:

$MgCl_2$	47·5 per cent.
Mg	30·0 „
H_2O	22·5 „

Let half the chlorine escape as HCl; 200 kilos. of the mass would then yield—

Cl	35·5 kilos.
HCl	36·5 „
H_2O (vapour)	36·0 „
MgO	100·0 „
	208·0 „

In addition, 8 kilos. of oxygen have been consumed from 200 cubic metres of atmospheric air introduced. To heat them to 1000° there will be required:

$$200 \times 0{\cdot}31 \times 1000 = 62000 \text{ heat-units.}$$

The 100 kilos. magnesia: $100 \times 0{\cdot}244 \times 1000 = 24400$ heat-units.

The chlorine $35{\cdot}5 \times 0{\cdot}12 \times 1000 = 4260$ heat-units.

The HCl: $36{\cdot}5 \times 0{\cdot}19 \times 1000 = 6935$ heat-units.

The water: $36\,[620 + (900{\cdot}0{\cdot}48)] = 37{\cdot}872$ heat-units.

For the evolution of 35·5 kilos. chlorine from magnesium chloride, there are required 3500, and for hydrochloric acid 10,000 heat-units. Hence results the following distribution of heat for each 35·5 kilos. of chlorine:

Chemical work	13·500	heat-units.
Heating air	62·000	,,
Magnesia	24·400	,,
Watery vapour	37·900	,,
Chlorine and hydrochloric acid . .	11·200	,,
	149·000	,,

In addition come the losses of conduction and radiation from the masonry. As nearly half the consumption of heat goes to heating the air, the regulation of the access of air is very important. It may be recommended to warm the air before its admission by means of the gases escaping, on the same principle as in the hot blast in iron-smelting. At the same time, the refrigerating apparatus would be relieved which has now to overcome 62,000 + 37,900 + 11,200 = 111,100 heat-units.

In working up calcium chloride, there result—

$$CaCl_2 + O = CaO + Cl_2$$
$$-170{,}230 + 131{,}360 = 38{,}870 \text{ heat-units, and}$$
$$CaCl_2 + H_2O = CaO + 2HCl$$
$$-170{,}230 - 57{,}000 + 131{,}360 + 44{,}000 = -51{,}870 \text{ heat-units.}$$

Hence, as regards the heat needed for its decomposition, calcium chloride is less advantageous than magnesium chloride.

In obtaining hydrochloric acid from sodium chloride and sulphuric acid, there is first formed bisulphate:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$-97{,}700 - 192{,}900 + 267{,}800 + 22{,}000 = -800 \text{ heat-units.}$$

The demand for heat is therefore almost *nil*. In the formation of monosulphate:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$
$$-195{,}400 - 192{,}900 + 328{,}500 + 44{,}000 = -15{,}800 \text{ heat-units.}$$

Hence the mixture must be heated to complete the reaction, as experience shows.

To calculate the heat required by a salt-cake furnace, let us suppose that the 98 kilos. sulphuric acid required to decompose 117 kilos. sodium chloride contain 30 kilos. of water, and that the hydrochloric acid escapes as a mean at 400°, the watery vapour at 500°, whilst the sulphate is heated to 600°.

If the specific heat of the salt-cake is assumed at 0·232, there are required to heat the 142 kilos. of salt-cake $142 \times 0{\cdot}232 \times 600 = 19{,}766$ heat-units. The specific heat of hydrochloric acid is, on the average, 0·19, therefore $73 \times 0{\cdot}19 \times 400 = 5{,}548$ heat-units. To convert water of 17° into steam at 500° there are required 812 heat-units—*i.e.*, for 30 kilos. 24,360 heat-units.

If we consider the draught of the chimney, &c., there may be reckoned in round numbers 500 heat-units for the work performed by the hydrochloric acid generated.

Hence—

Heating sulphate	19,766	heat-units.
„ hydrochloric acid	5,548	„
„ watery vapour	24,360	„
Chemical work	15,800	„
Mechanical work	500	„
Together about	66,000	„

In the condensation of the hydrochloric acid, there have to be removed by refrigeration:

Watery vapour	24,360	heat-units.
HCl specific heat	5,548	„
HCl solution heat	15,000	„
	45,000	„

It is here supposed that the watery vapour is condensed, but not the fire-gases.

These figures merely show in what manner such calculations may be conducted on analytical data.

In accordance with the easy execution of the oxidation of Weldon mud, it is conducted with a development of heat, as the formation of the manganous hydrate yields 94,770, and that of the hydrated peroxide 116,280 heat-units.

The decomposition of the latter with strong hydrochloric acid gives—

$$MnO_3H_2 + 4HCl.aq. = MnCl_2.aq. + Cl_2 + 3H_2O$$
$$-116{,}300 = 148{,}000 + 128{,}000 + 205{,}200 = 68{,}900 \text{ heat-units.}$$

As soon as the mixture is raised to the temperature of the reaction the liberation of Cl goes on readily.

The thermic relations of the manufacture of chloride of lime have not been determined, though it is known that in the formation of potassium hypochlorite in an aqueous solution 24,600 heat-units are liberated according to the reaction

$$2KOH.aq. + Cl_2 = KCl.aq. + KOCl.aq.$$

In the formation of potassium chlorate in an aqueous solution there are liberated:

$$6KOH.aq. + 3Cl_2.aq. = 5KCl.aq. + KClO_3.aq.$$

that is, 97,900 heat-units, a renewed proof that the reactions which give most heat are not always most easy to conduct.

The following works may be consulted:—J. Thomsen, *Thermochem. Untersuchungen* (Leipzig, 1882 to 1888). Berthelot, *Essai de mécanique chimique* (Paris, Dunod, 1879). Al. Naumann, *Handbuch der Thermochemie* (Brunswick, 1882). Horstmann, *Theoretische Chemie*. W. Ostwald, *Verwandtschafts Lehre* (Leipzig, 1887).

SECTION IV.

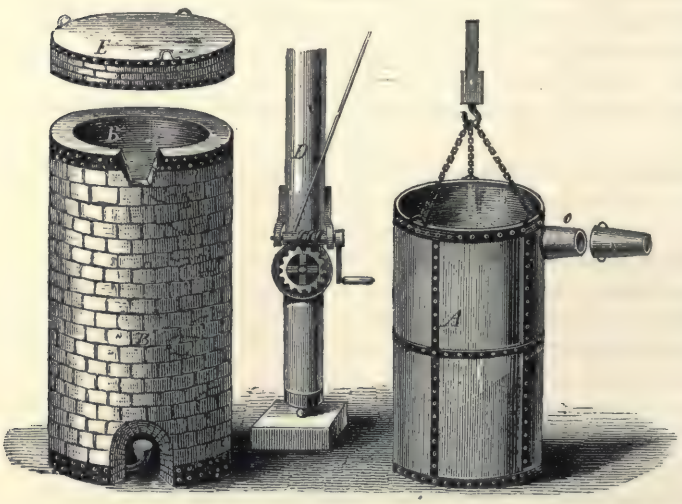
THE ORGANIC CHEMICAL MANUFACTURES.

ALCOHOLS AND ETHERS.

Methylic Alcohol.—$CH_3.OH$, a liquid boiling at 65·5° to 66°, is formed on the dry distillation of wood. Leaf-bearing trees yield it in larger proportion than the conifers.

For the distillation there are commonly used horizontal iron retorts, heated in the same manner as gas retorts, though in general not above 500°. Occasionally, large upright retorts are used, or, in France, cylinders of sheet-iron (Fig. 377). Such a cylinder, *A*, has in its upper half an opening *o*, to which a connecting-piece is screwed on. Upon the cylinder is laid the cover, which is screwed fast as soon as the cylinder has been filled with wood. The cylinder itself is lowered by means of the crane, *D*, into a cylindrical furnace, *B*, closed above with the stone cover, *E*. The products given off on the application of heat pass through the pipe, *b* (Fig. 378), which is connected with the cylinder and bent in a zigzag manner, through the refrigerating apparatus *c*, set in the support *d*, to which cold water is conveyed through *f*, whilst the heated water escapes at *k*. Acetic acid, tar, and wood-spirit are liquified, and flow into the vat *g*, in which the tar is chiefly deposited. The lighter liquids run through *m* to the second vat, *h*. The combustible gases escape through the pipe *i*, into the open air, or into the furnace, though their value as fuel is but small. In large works there are used, instead of the wooden vats, cisterns of cement or masonry sunk into the ground, each being connected with the next following by a pipe at its upper end. The bulk of the tar collects in the first cistern, whilst the wood-vinegar, freed from the tar, which is merely mechanically suspended, flows into the last cistern. Wood-gas works, of course, produce wood-vinegar as a bye-product.

Fig. 377.

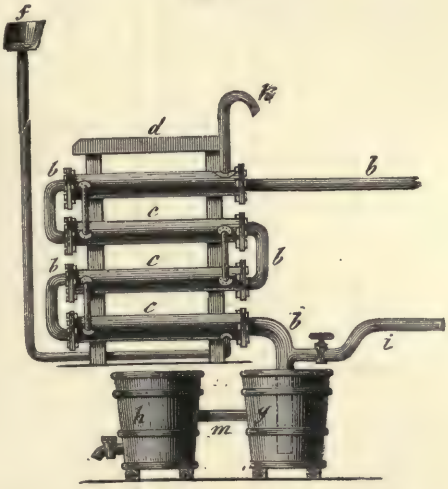


The watery liquid separated from the tar contains methylic alcohol, acetone, acetic acid, &c., and is distilled. Crude wood-spirit first passes over and then acetic acid, which

is neutralised with lime. The wood-spirit is purified by rectification in the column apparatus.

In order to remove the last portion of acetone, the purified wood-spirit is treated with chlorine and rectified again. Oak-wood yields on distillation 1 per cent. of wood-spirit.

Fig. 378.



The proportion of methyl alcohol in commercial wood-spirit is ascertained by converting it into methyl iodide by phosphorus di-iodide (PI_2); 5 c.c. of absolute methyl alcohol yield 7·19 c.c. methyl iodide.

Uses.—Crude wood-spirit is used for denaturising spirits; pure methyl alcohol is used in the manufacture of coal-tar colours and in ice-machines, after conversion into ether.

Ethyl Alcohol (ordinary alcohol), $C_2H_5.OH$. The production of alcohol by fermentation will be described below. It is obtained in the anhydrous state by distillation over quicklime. Pure alcohol boils at 78°.

The determination of the percentage composition of samples of alcohol is effected by means of the sp. gr. For technical purposes hydrometers are used. Hitherto the hydrometers or areometers of Tralles and Richter have been most in use. That of Stoppani agrees with the latter. Both are percentage hydrometers—*i.e.*, they show by the number down to which they sink how much pure alcohol is contained in the liquid in question. The difference between the two instruments is that the hydrometer of Tralles indicates percentages by volume, and that of Richter percentages by weight. As the graduation of the Richter hydrometer proceeds from inaccurate assumptions that of Tralles is to be preferred.* The hydrometer of Tralles has been until quite lately the legally recognised instrument in Germany for determining percentages of alcohol, though one which gives percentages by weight has now been introduced in its place.

Spirits intended for technical purposes are exempted from duty if they are denaturised by any one of a variety of methods which the manufacturer may select. The most suitable of all these agents is "Dippel's animal oil." The alcohol tables of O. Hehner, which give the proportion of alcohol for different sp. gr. at 15·5°, are here given as far as they are important in analysis and the arts.

* In England the hydrometer of Sykes is in official use.

Specific Gravity = 15·5°.	Absolute Alcohol.		Specific Gravity = 15·5°.	Absolute Alcohol.		Specific Gravity = 15·5°.	Absolute Alcohol.	
	Weight.	Volume.		Weight.	Volume.		Weight.	Volume.
	Per Cent.	Per Cent.		Per Cent.	Per Cent.		Per Cent.	Per Cent.
1·0000	0·00	0·00	0·9878	7·40	9·21	0·9758	16·62	20·43
0·9998	0·11	0·13	6	7·53	9·37	6	16·77	20·61
6	0·21	0.26	4	7·67	9·54	4	16·92	20·80
4	0·32	0·40	2	7·80	9·70	2	17·08	20·99
2	0·42	0·53	0	7·93	9·86	0	17·25	21·19
0	0·53	0·66						
			0·9868	8·07	10·03	0·9748	17·42	21·39
0·9988	0·63	0·79	6	8·21	10·21	6	17·58	21·59
6	0·74	0·93	4	8·36	10·38	4	17·75	21·79
4	0·84	1·06	2	8·50	10·56	2	17·92	21·99
2	0·95	1·19	0	8·64	10·73	0	18·08	22·18
0	1·06	1·34						
			0·9858	8·79	10·91	0·9738	18·23	22·36
0·9978	1·19	1·49	6	8·93	11·08	6	18·38	22·55
6	1·31	1·65	4	9·07	11·26	4	18·54	22·73
4	1·44	1·81	2	9·21	11·44	2	18·69	22·92
2	1·56	1·96	0	9·36	11·61	0	18·85	23·10
0	1·69	2·12						
			0·9848	9·50	11·79	0·9728	19·00	23·28
0.9968	1·81	2·27	6	9·64	11·96	6	19·17	23·48
6	1·94	2·43	4	9·79	12·13	4	19·33	23·68
4	2·06	2·58	2	9·93	12·31	2	19·50	23·88
2	2·17	2·72	0	10·08	12·49	0	19·67	24·08
0	2·28	2·86						
			0·9838	10·23	12·68	0·9718	19·83	24·28
0·9958	2·39	3·00	6	10·38	12·87	6	20·00	24·48
6	2·50	3·14	4	10·54	13·05	4	20·17	24·68
4	2·61	3·28	2	10.69	13·24	2	20·33	24·88
2	2·72	3·42	0	10·85	13·43	0	20·50	25·07
0	2·83	3·55						
			0·9828	11·00	13·62	0·9708	20·67	25·27
0·9948	2·94	3·69	6	11·15	13·81	6	20·83	25·47
6	3·06	3·83	4	11·31	13·99	4	21·00	25·67
4	3·18	3·98	2	11·46	14·18	2	21·15	25·86
2	3·29	4·12	0	11·62	14·37	0	21·31	26·04
0	3·41	4·27						
			0·9818	11·77	14·56	0·9698	21·46	26·22
0·9938	3·53	4·42	6	11·92	14·74	6	21·62	26·40
6	3·65	4·56	4	12·08	14·93	4	21·77	26·58
4	3·76	4·71	2	12·23	15·12	2	21·92	26·77
2	3·88	4·85	0	12·38	15·30	0	22·08	26·95
0	4·00	5·00						
			0·9808	12·54	15·49	0·9688	22·23	27·13
0·9928	4·12	5·16	6	12·69	15·68	6	22·38	27·31
6	4·25	5·32	4	12·85	15·86	4	22·54	27·49
4	4·37	5·47	2	13·00	16·05	2	22·69	27·68
2	4·50	5·63	0	13·15	16·24	0	22·85	27·86
0	4·62	5·78						
			0·9798	13·31	16·43	0·9678	23·00	28·04
0·9918	4·75	5·94	6	13·46	16·61	6	23·15	28·22
6	4·87	6·10	4	13·62	16·80	4	23·31	28·41
4	5·00	6·24	2	13·77	16·98	2	23·46	28·59
2	5·12	6·40	0	13·92	17·17	0	23·62	28·77
0	5·25	6·55						
			0.9788	14·09	17·37	0·9668	23·77	28·95
0·9908	5·37	6·71	6	14·27	17·59	6	23·92	29·13
6	5·50	6·86	4	14·45	17·81	4	24·08	29·31
4	5·62	7·01	2	14·64	18·03	2	24·23	29·49
2	5·75	7·17	0	14·82	18·25	0	24·38	29·67
0	5·87	7·32						
			0·9778	15·00	18·48	0·8418	82·62	87·61
0·9898	6·00	7·48	6	15·17	18·68	6	82·69	87·67
6	6·14	7·66	4	15·33	18·88	4	82·77	87·73
4	6·28	7·83	2	15·50	19·08	2	82·85	87·79
2	6·43	8·01	0	15·67	19·28	0	82·92	87·85
0	6·57	8·18						
			0·9768	15·83	19·49	0·8408	83·00	87·91
0·9888	6·71	8·36	6	16·00	19·68	6	83·08	87·97
6	6·86	8·54	4	16·15	19·87	4	83·15	88·03
4	7·00	8·72	2	16·31	20·06	2	83·23	88·09
2	7·13	8·88	0	16 46	20·24	0	83·31	88·16
0	7·27	9·04						

Specific Gravity = 15·5°.	Absolute Alcohol.		Specific Gravity = 15·5°.	Absolute Alcohol.		Specific Gravity = 15·5°.	Absolute Alcohol.	
	Weight.	Volume.		Weight.	Volume.		Weight.	Volume.
	Per Cent.	Per Cent.		Per Cent.	Per Cent.		Per Cent.	Per Cent.
0·8398	83·38	88·22	0·8278	88·04	91·81	0·8158	92·52	95·08
6	83·46	88·28	6	88·12	91·87	6	92·59	95·13
4	83·54	88·34	4	88·20	91·93	4	92·67	95·19
2	83·62	88·40	2	88·28	91·99	2	92·74	95·24
0	83·69	88·46	0	88·36	92·05	0	92·81	95·29
0·8388	83·77	88·52	0·8268	88·44	92·12	0·8148	92·89	95·35
6	83·85	88·58	6	88·52	92·18	6	92·96	95·40
4	83·92	88·64	4	88·60	92·24	4	93·04	95·45
2	84·00	88·70	2	88·68	92·30	2	93·11	95·50
0	84·08	88·76	0	88·76	92·36	0	93·18	95·55
0·8378	84·16	88·83	0·8258	88·84	92·42	0·8138	93·26	95·61
6	84·24	88·89	6	88·92	92·48	6	93·33	95·66
4	84·32	88·95	4	89·00	92·54	4	93·41	95·71
2	84·40	89·01	2	89·08	92·60	2	93·48	95·76
0	84·48	89·08	0	89·16	92·66	0	93·55	95·82
0·8368	84·56	89·14	0·8248	89·23	92·71	0·8128	93·63	95·87
6	84·64	89·20	6	89·31	92·77	6	93·70	95·92
4	84·72	89·27	4	89·38	92·83	4	93·78	95·97
2	84·80	89·33	2	89·46	92·89	2	93·85	96·03
0	84·88	89·39	0	89·54	92·94	0	93·92	96·08
0·8358	84·96	89·46	0·8238	89·62	93·00	0·8118	94·00	96·13
6	85·04	89·52	6	89·69	93·06	6	94·07	96·18
4	85·12	89·58	4	89·77	93·11	4	94·14	96·22
2	85·19	89·64	2	89·85	93·17	2	94·21	96·27
0	85·27	89·70	0	89·92	93·23	0	94·28	96·32
0·8348	85·35	89·75	0·8228	90·00	93·29	0·8108	94·34	96·36
6	85·42	89·81	6	90·07	93·34	6	94·41	96·41
4	85·50	89·87	4	90·14	93·39	4	94·48	96·46
2	85·58	89·93	2	90·21	93·44	2	94·55	96·50
0	85·65	86·99	0	90·29	93·49	0	94·62	96·55
0·8338	85·73	90·05	0·8218	90·36	93·54	0·8098	94·69	96·60
6	85·81	90·11	6	90·43	93·59	6	94·76	96·64
4	85·88	90·17	4	90·50	93·64	4	94·83	96·69
2	85·96	90·23	2	90·57	93·70	2	94·90	96·74
0	86·04	90·29	0	90·64	93·75	0	94·97	96·78
0·8328	86·12	90·35	0·8208	90·71	93·80	0·8088	95·04	96·83
6	86·19	90·40	6	90·79	93·85	6	95.11	96·88
4	86·27	90·46	4	90·86	93·90	4	95·18	96·93
2	86·35	90·52	2	90·93	93·95	2	95·25	96·98
0	86·42	90·58	0	91·00	94·00	0	95·32	97·02
0·8318	86·50	90·64	0·8198	91·07	94·05	0·8078	95·39	97·07
6	86·58	90·70	6	91·14	94·10	6	95·46	97·12
4	86·65	90·76	4	91·21	94·15	4	95·54	97·17
2	86·73	90·82	2	91·29	94·21	2	95·61	97·22
0	86·81	90·88	0	91·36	94·26	0	95·68	97·27
0·8308	86·88	90·93	0·8188	91·43	94·31	0·8068	95·75	97·32
6	86·96	90·99	6	91·50	94·36	6	95·82	97·37
4	87·04	91·05	4	91·57	94·41	4	95·89	97·4
2	87·12	91·11	2	91·64	94·46	2	95·96	97·46
0	87·19	91·17	0	91·71	94·51	0	96·03	97·51
0·8298	87·27	91·23	0·8178	91·79	94·56	0·8058	96·10	97·55
6	87·35	91·28	6	91·86	94·61	6	96·16	97·60
4	87·42	91·34	4	91·93	94·66	4	96·23	97·64
2	87·50	91·40	2	92·00	94·71	2	96·30	97·68
0	87·58	91·46	0	92·07	94·76	0	96·37	97·73
0·8288	87·65	91·52	0·8168	92·15	94·82	0·8048	96·43	97·77
6	87·73	91·57	6	92·22	94·87	6	96·50	97·81
4	87·81	91·63	4	92·30	94·92	4	96·57	97·86
2	87·88	91·69	2	92·37	94·98	2	96·63	97·90
0	87·96	91·75	0	92·44	95·03	0	96·70	97·94

Specific Gravity = 15·5°.	Absolute Alcohol.		Specific Gravity = 15·5°	Absolute Alcohol.		Specific Gravity = 15·5°.	Absolute Alcohol.	
	Weight.	Volume.		Weight.	Volume.		Weight.	Volume.
	Per Cent.	Per Cent.		Per Cent.	Per Cent.		Per Cent.	Per Cent.
0·8038	96·76	97·98	0·8002	97·96	98·76	0·7968	99·03	99·39
6	96·83	98·03	0	98·03	98·80	6	99·10	99·43
4	96·90	98·07	0·7998	98·09	98·83	4	99·16	99·47
2	96·96	98·11	6	98·16	98·87	2	99·23	99·51
0	97·03	98·16	4	98·22	98·91	0	99·29	99·55
0·8028	97·10	98·20	2	98·28	98·94	0.7958	99·36	99·59
6	97·16	98·24	0	98·34	98·98	6	99·42	99·63
4	97·23	98·29	0·7988	98·41	99·02	4	99·48	99·67
2	97·30	98·33	6	98·47	99·05	2	99·55	99·71
0	97·37	98·37	4	98·53	99·09	0	99·61	99·75
0·8018	97·43	98·42	2	98·59	99·13	0·7948	99·68	99·80
6	97·50	98·46	0	98·66	99·16	6	99·74	99·84
4	97·57	98·50	0·7978	98·72	99·20	4	99·81	99·88
2	97·63	98·54	6	98·78	99·24	2	99·87	99·92
0	97·70	98·59	4	98·84	99·27	0	99·94	99·96
0·8008	97·76	98·63	2	98·91	99·31	0·7938	100·00	100·00
6	97·83	98·67	0	98·97	99·35			
4	97·90	98·71						

Chloroform, $CHCl_3$, a colourless liquid, boiling at 61°, is obtained by distilling alcohol with chloride of lime. For this purpose there are used iron vessels, of about 1·4 metres in height and 2 metres in diameter. They are fitted with a mechanical agitator, a pipe for introducing steam and one for water, and a manhole for filling in the chloride of lime. At the upper margin of the generator there is placed a perforated lead tube (the holes towards the cylinder), which is connected with the water-supply. A pipe of 75 mm. inside diameter, with a strong decline, leads to the condenser. It is best to use 4 parts chloride of lime of 103° to 108° (higher and lower qualities are less suitable), 3 parts alcohol at 96° Tralles in 13 parts of water, so that we have 16 parts of liquid to 4 parts of solid matter. For a daily output of 115 kilos. of chloroform, each of the four generators must have a charge of 400 kilos. chloride of lime, 300 kilos. alcohol, and 1300 kilos. of water. The alcohol is first introduced, then water enough to make up 1600 litres of liquid, next the agitator is set in action, and the 400 kilos. of chloride of lime are added. The apparatus is then closed air-tight, and the mixture is heated by means of steam. As soon as the thermometer reaches 40° the steam is shut off. The agitator is worked until the thermometer reaches 45°, when it is disconnected. The temperature still rises slowly, and the reaction reaches its height at about 60°. In very hot weather the temperature rises much higher, and in that case cold water is let flow over the apparatus. Between the receiver and the refrigerator there is a glass-tube introduced in the connecting-pipe. As soon as the reaction is in progress, a fine rain of chloroform, alcohol, and water is seen to drive through this tube. As the air which issues from the apparatus is saturated with the vapour of chloroform, it is caused, before escaping, to pass through a washing bottle filled with water. This violent "blowing" lasts about a minute, when the chloroform begins to flow. As soon as about 30 kilos. have been distilled off from each apparatus the agitator is again set in motion. When the chloroform no longer separates as a heavy layer in the distillate, the tin vessels which serve as receivers are charged. The distillate which next follows consists of alcohol saturated with chloroform, and it is collected as long as chloroform separates out after shaking with water. As soon as the distillate becomes clear after shaking, the efflux cocks are closed, and the distillate runs into the pressure-vessels. The agitator is kept in motion to prevent the solid matter from settling, and the distillation is kept up until the distillate marks only 3° Tralles. The lime liquor is then let off through a hole near the bottom. In

each pressure-vessel there are now contained 500–600 litres of very dilute alcohol. Before a new operation is commenced, it is calculated accurately how much alcohol is present and how much liquid. If there are between 270 and 300 kilos. of alcohol in the pressure-vessel it is only made up to 300 kilos. The quantity of liquid still required is calculated and run into the generator, whilst the chloride of lime is stirred up. When this has been done the generators are closed air-tight, and the contents of the pressure-vessels are forced into them. The turbid alcoholic chloroform which distils over first on washing after rectification is collected separately and washed again.

According to Günther, the carbonic acid formed from the oxidation of the alcohol initiates the production of chloroform by setting free hypochlorous acid:

1. $CaO_2Cl_2 + CO_2 + H_2O = 2HOCl + CaCO_3$.
2. $C_2H_6O + HOCl = C_2H_4O + HCl + H_2O$.
3. $HCl + HOCl = 2Cl + H_2O$.
4. $C_2H_4O + 6Cl = CCl_3COH + 3HCl$.
5. $CCl_3COH + CaO_2H_2 = 2CHCl_3 + Ca(HCOO)_2$.

In the production of iodoform, CHI_3, the same author recommends mixing alcohol containing 20 to 25 parts of aldehyde with 10 parts solution of soda and then to introduce iodine. The mixture is allowed to stand at the common temperature with occasional stirring until the separation of iodoform has begun; perhaps it is advantageous to add here a little sodium iodide at the outset. The formation of iodoform is explained by the following formulæ:—

1. $Na_2CO_3 + 2I + H_2O = HOI + NaI + NaHCO_3$.
2. $C_2H_6O + HOI = C_2H_4O + HI + H_2O$.
3. $HI + HOI = 2I + H_2O$.
4. $C_2H_4O + 6I + 3HOI = CI_3(COH) + 6I + 3H_2O$.
5. $CI_3(COH) + NaHCO_3 = CHI_3 + NaHCOO + CO_2$.

Chloral hydrate, $C_2HCl_3O.H_2O$, is obtained by passing chlorine into alcohol. If heated with potassa-lye it yields pure chloroform:

$$C_2HCl_3O + KOH = CHCl_3 + KCHO_2.$$

Ether (C_2H_5O) boils at 35·5°. It is obtained by distilling alcohol with sulphuric acid:

$$C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O, \text{ and}$$
$$C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$

As the sulphuric acid is constantly re-constituted, whilst ether and water distil off, alcohol is let constantly flow in as fast as it is decomposed.

ORGANIC ACIDS.

Among the organic acids which are not obtained from tar the following are technically the most important.

Acetic Acid.—$H.C_2H_3O_2$ is formed by the oxidation of ethyl-alcohol by atmospheric oxygen. Aldehyde is first formed, and on taking up one atom oxygen it becomes acetic acid—

$$C_2H_6O + O = C_2H_4O + H_2O; \; C_2H_4O + O = C_2H_4O_2; \text{ or}$$
$$CH_3.CH_2OH + O_2 = CH_3.COOH + H_2O.$$

46 kilos. ethyl-alcohol consequently require 32 kilos. or 22·3 cubic metres of oxygen (= 107 cubic metres of atmospheric air) in order to yield 60 kilos. of pure acetic acid

The following kinds of vinegar are distinguished by their origin:—

1. Wine vinegar, containing in addition to acetic acid, almost all the constituents of wine—*e.g.*, tartaric acid, succinic acid, glycerine, and certain others which give it an agreeable aroma.

2. Spirit vinegar, which generally consists of a mixture of acetic acid and water with small quantities of aldehyde and acetic ether.

3. Fruit vinegars, obtained from cyder and perry or direct from apples, contain, along with acetic acid, malic acid (and have the aroma of ripe apples).

4. Beer, malt, or grain vinegar, made from unhopped beer-worts (or sometimes, under the name of alegar, from spoiled beer). It contains, along with acetic acid and small quantities of aldehyde, extractive matter, phosphates, nitrogenous matter and dextrine (which may be the cause of its want of aroma).

5. Sugar vinegar, made from solutions of cane-sugar or cane-treacle. It is probable that with the addition of the proper vinous ferments a true wine vinegar might be obtained from this source. Vinegar is also made from sugar-beets.

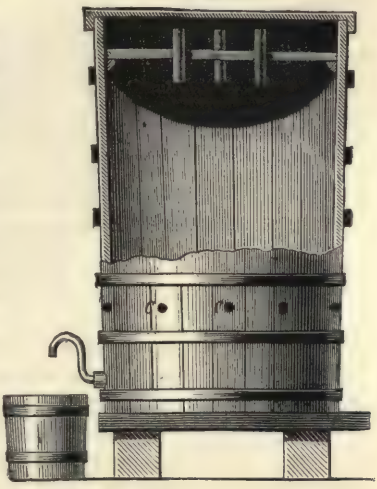
6. Vinegar is also obtained from pyroligneous acid, after elimination of the tarry matters, and acetose.

The Older Method of Vinegar Making.—As regards the so-called old method of vinegar making it is without doubt an imitation of the spontaneous souring of beer, wine, and fermented liquors generally, and under conditions which are conducive to the improvement of the product; such conditions are—a suitable temperature, intimate contact of the souring liquor with air, and a so-called acetification inducing ferment. This method is very generally employed for making wine vinegar—French vinegar as it is termed in England—but may of course be used for malt or fruit vinegar making as well. Generally a "souring" vessel or "mother" vessel made of oak wood is employed; this vat is first, when newly made, thoroughly scalded with boiling water, and when thereby the extractive matter of the wood is exhausted the vessel is filled with boiling vinegar; when the wood is soaked with vinegar there is poured into the vessel one hectolitre of wine, and after eight days again 10 litres of wine are added, and this operation continued weekly until the vessel is filled for two-thirds of its cubic capacity. About fourteen days after the last addition of the wine the whole of the contents will have become converted into vinegar. Half this quantity is withdrawn from the souring vessel and carried to the store; to the remainder more wine is added, and the preparation of vinegar proceeded with uninterruptedly by the operation described. A souring vessel may continue to serve its purpose for six years, and often longer, but generally at the end of this time there is collected in the vessel so large a quantity of yeast sediment, argol, stone, and other matter, as to render the thorough cleansing of the vessel necessary; after this operation it is again fit for further use. Although it might appear that in this process of acetification there is no great contact of air, and the fluid is apparently quite at rest, there is a constant change of the particles of the surface of the fluid, owing to the fact that every drop of vinegar formed sinks to the bottom of the vessel, or at least below the surface, owing to its increased specific gravity; while as regards the air, that portion of it from which the oxygen has been absorbed by becoming specifically lighter (0.9 sp. gr.) has a tendency to rise upwards, and to be replaced by heavier air (1·0 sp. gr.); thus a constant circulation of air is provided.

Quick Vinegar Making.—The so-called quick vinegar process, founded on an older method of vinegar preparation suggested by Boerhaave in 1720, was first introduced by Schutzenbach in 1823. The chief principle of this method consists in causing the fluid, generally brandy, to be converted into vinegar by ultimate contact with the atmosphere at the requisite temperature; or, in other words, the oxidation of the alcohol to acetic acid is effected in the shortest time and with the least possible loss. The intimate contact of the fluid with the air is effected by:—1. Increasing the quantity of air admitted by means of a continual current of air, made to meet the drops of the fluid intended to be converted into vinegar, in the opposite direction to that in which these drops fall downwards. 2. By causing the liquid to be operated upon to trickle down drop by drop. A peculiarly constructed vessel is required for this operation; according to the strength of vinegar desired to be made two or four of these vessels

are employed, these constituting a group, or battery as it is termed. A sectional view of such a vessel is exhibited in Fig. 379; it is made of stout oaken staves, the vat being from 2 to 4 metres in height, and from 1 to 1·3 in width; at a height of from 20 to 30 centimetres from the bottom of the vessel are bored, at equal distances from each other, six holes—air-holes—of about 3 centimetres in diameter, so cut that the inner mouth of the hole is situated a little deeper than the outer; that is to say, the holes are bored towards the bottom in a slightly sloping direction. About one-third of a metre above the real lower bottom a false bottom is placed, similar in construction to a sieve, and at a height of a centimetre above the air-holes; upon the false bottom is a layer of beech-wood shavings extending upwards to about from 15 to 20 centimetres below the upper edge of the vat. The false bottom is sometimes constructed of laths of wood, forming a kind of gridiron-like network. Before their application the wood shavings are thoroughly washed with hot water and afterwards dried. The tub is then nearly filled with the dry wood shavings, which are next "soured." For this purpose warm vinegar is poured over them, and allowed to remain in contact with the wood for twenty-four hours, so as to cause the acetic acid to soak into the wood. At from 18 to 24 centimetres below the upper edge of the vat is fixed a perforated wooden disc, the holes of which are as large as a goose-quill, and are bored from 3 to 5 centimetres apart from each other. In order that the liquid intended to be converted into acetic acid may trickle slowly, and in fine spray as it were, over the wood shavings or thin chips of wood, through the holes, strings of twine or loosely spun cotton yarn are passed so as to penetrate downwards for a length of 3 centimetres, while at the top a knot is tied which prevents the strings slipping through the holes; by the action of the liquid, dilute spirits of wine usually, which is poured into the vessel, the twine becomes more or less swollen, and thereby obstructs the passage of the fluid so as to divide it into constantly trickling drops. The sieve bottom is fitted with from five to eight larger holes, each about 3 to 6 centimetres wide, which by means of glass tubes, each of from 10 to 15 centimetres in length, inserted and firmly fastened therein, act as draught tubes, so placed that no liquid can pass through them. The vat is covered at the top with a tightly-fitting wooden lid, in the centre of which a circular hole is cut, which serves as well for the purpose of pouring the liquid into the vessel as for the outlet of the air which enters the vessel from below. In consequence of the absorption of the oxygen so much heat is generated in the interior of the vessel that the air streams strongly upwards, causing fresh air to enter by the lower air-holes.

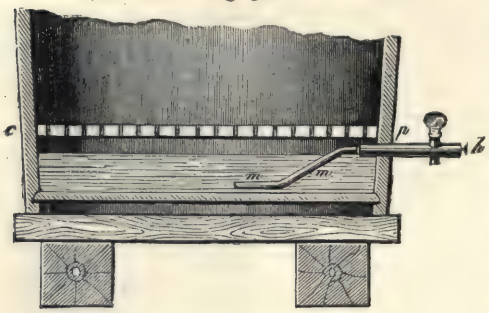
Fig. 379.



After the vinegar tub has been soured the fluid to be converted into vinegar—generally brandy, more rarely malt liquor or wine—is poured in; the fluid flowing off from the first vessel is poured into the second, and if the original liquid did not contain more than from 3 to 4 per cent. of alcohol, the fluid which runs off from the second vessel will be completely converted into good vinegar. The vinegar collects between the true and false bottoms. As will be seen from the woodcut the vinegar cannot flow out until its level is equal to that of the mouth of the glass tube. In consequence of this arrangement a layer of about 16 to 20 centimetres in depth of warm vinegar assists in the acetification by the evolution of acid vapours which ascends into the fluid above. The tube must dip into the lower part of the fluid in the interior of the tub, as it is

there that the specifically heavier vinegar collects. The arrangement will be readily understood from Fig. 380; *c p* is the perforated bottom, just below which is situated the wooden tap *h*, fastened to the bent glass tube, *m m*, the free open end of which touches the bottom of the tub.

Fig. 380.



Recently (1868) Singer's vinegar generator has been introduced. It consists of a number of vessels, one placed above the other, and so connected together by wooden tubes that the liquid intended to be converted into vinegar trickles drop by drop from the one vessel into another; in each tube is cut a longitudinal slit, through which air freely circulates; the apparatus is placed in a suitably constructed shed, wherein a convenient temperature is kept up and from which draught is excluded. By means of this apparatus the loss of alcohol experienced in the use of the vats above mentioned is prevented. Singer's apparatus is fully described in the *Jahresbericht der Chem. Technologie*, 1868, p. 580.

The composition of the fluid to be acetified varies very much; one of the mixtures very generally used is made up of 20 litres of brandy of 50 per cent. Tralles, 40 litres of vinegar, and 120 litres of water, to which is first added a liquid, made by soaking a mixture of bran and rye meal in water in order to promote the formation of the vinegar fungus (*Mycoderma aceti*). The room in which the vats are placed should be heated to 20° to 24°; the temperature in the vats rises to 36° and more; consequently the alcohol, aldehyde, and acetic acid are volatilised, and this loss may amount to about one-tenth. Taking this loss into account we may assume that 1 hectolitre of brandy at 50 per cent. Tralles (= 42 per cent. according to weight) yields by weight—

13·0	hectolitres	of vinegar	of 3	per cent.	acetic acid.
9·9	,,	,,	4	,,	,,
7·9	,,	,,	5	,,	,,
6·6	,,	,,	6	,,	,,
5·6	,,	,,	7	,,	,,
4·9	,,	,,	8	,,	,,
4·4	,,	,,	9	,,	,,
3·9	,,	,,	10	,,	,,

When required for transport it is, of course, most advantageous to prepare very strong vinegar which (at the place where it is to be consumed) can be diluted with the requisite quantity of water.

In this process it is very essential that the shavings should be uniformly moistened. Rose therefore omits the strings, and places over the bottom a rocking-trough, which pours out the liquid alternately on each side of the false bottom. The distribution may be better effected by means of Segner's wheel.

In the process of Michaelis acetification is effected in rotating tubs.

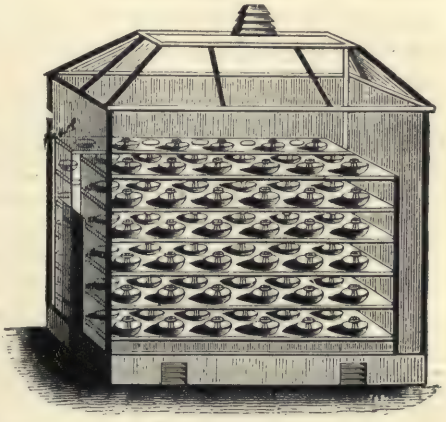
Pasteur has referred the formation of vinegar from alcohol to the action of bacteria, and in 1862 described a physiological process for the manufacture. A fungus (*Mycoderma aceti*) is the agent. This fungus is first propagated in a fluid, consisting of water and 2 per cent. of alcohol with 1 per cent. of vinegar and a small quantity of potassium, calcium, and magnesium phosphate. The small plant soon spreads itself over the entire surface of the fluid, without leaving the smallest space uncovered. At the same time the alcohol is acetified. As soon as half the alcohol is converted into vinegar, small quantities of wine or alcohol mixed with beer are added daily. When the acetification becomes

weaker, the complete conversion of the free alcohol still present in the fluid is allowed to take place. The vinegar is then drawn off and the plant again employed in the same apparatus. Vinegar prepared by this method possesses much of the aroma characteristic of wine vinegar. An essential condition to the rapid formation of vinegar by this method is a strong development of the plant. A vessel with 1 square metre of surface, and capable of containing 50 to 100 litres of fluid, yields daily 5 to 6 litres of vinegar. The vessels are circular or rectangular wooden tanks, with but a slight depth, and covered with lids. At the ends are bored two small openings for the entrance of the air. Two tubes of gutta-percha, pierced laterally with small holes, are carried down to the bottom of the tank, and used to pour alcohol into the tank without opening the lid. The tank which Pasteur employed had a surface of 1 square metre and a depth of 20 centimetres. He found phosphates and ammonia necessary for the growth of the plant. When wine or malt liquor, &c., is employed, these substances are present therein in sufficient quantity; but when only alcohol is used, ammonium sulphate, potassium phosphate, and magnesia are added in such quantity that the fluid contains $\frac{1}{10000}$th of this saline mixture, to which also some vinegar is added. It has been long known that the addition of bread, flour, malt, and raisins to alcoholic fluids about to be acetified greatly promotes the formation of vinegar, as these substances contain the requisite organic and inorganic food suited for the propagation of the vinegar fungus.

According to this method a manufactory for wine vinegar was established in Orleans in 1871, and in 1879 E. Wurm erected similar works at Breslau. He used large wooden vats, charged with 200 litres of the vinegar mixture, consisting of water, alcohol, and acetic acid, along with the nutritive salts recommended by Pasteur; *i.e.*, potassium phosphate, 0·01 per cent.; calcium phosphate, 0·01 per cent.; magnesium phosphate, 0·01 per cent.; ammonium phosphate, 0·02 per cent. The vats are closely covered with wooden lids. Air is admitted through small holes at the sides. The fungus is sown by means of a small, thin wooden spatula. The main conditions are: a pure ferment, uniform temperature of 30°, and a regulated inflow of alcohol. This process has not become more widely used, as its production was not sufficiently abundant.

Vinegar by means of Platinum Black.—Dobereiner was the first who pointed out that, with the aid of platinum black, alcoholic vapours could be acetified in a very short time; and to this process the following apparatus is especially adapted. Fig. 381 shows a small glass house, in the interior of which are seen a number of compartments. The shelves forming these compartments support a number of porcelain capsules. The alcohol to be acetified is poured into these capsules, in each of which is placed a tripod, also of porcelain, supporting a watch-glass containing platinum black, or spongy platinum. In the roof and at the bottom of the apparatus are ventilators, so constructed as to admit of regulating access of air. By means of a small steam pipe the interior of the house is heated to 33°. By this means the alcohol is gently evaporated, and coming into contact with the platinum black or sponge, is acetified. So long as the ventilation is maintained, the platinum black retains its property of oxidising the alcohol. With an apparatus of 40 cubic metres capacity and with 17 kilos. of platinum

Fig. 381.



black, 150 litres of alcohol can daily be converted into pure vinegar. If it be desired to prepare the vinegar without any loss of alcohol, it becomes necessary to pass the outgoing air through a condenser in order to collect the vapours of alcohol and acetic acid which otherwise would be carried off.

Properties and Examination of Vinegar, Acetometry.—The value of a vinegar is dependent upon its flavour and upon its strength, or upon the quantity of acetic acid it contains. According to its containing more or less acetic acid the vinegar tastes more or less sour. The colour varies with the fluid from which the vinegar has been prepared; wine vinegar is of a yellow or red-yellow colour, fruit vinegar exhibits a golden colour, brandy vinegar is colourless, but as a rule the latter is coloured with caramel in imitation of wine vinegar. Freshly made vinegar contains, besides small quantities of unconverted alcohol, some aldehyde, which always occurs largely in vinegar not properly prepared. Recently it has become customary to add a small quantity of glycerine to the prepared vinegar.

The quantity of acetic acid contained in a vinegar depends upon the alcoholic contents of the fluid to be acetified, and also upon the more or less perfect conversion of the alcohol into acetic acid. Malt vinegar contains from 2 to 5 per cent., brandy vinegar from 3 to 6 per cent., wine vinegar from 6 to 8 per cent. of acetic acid. The sp. gr. of various kinds of vinegars differs from 1·010 to 1·030; the more alcohol a vinegar contains the lighter is it, the more extractive matter the heavier.

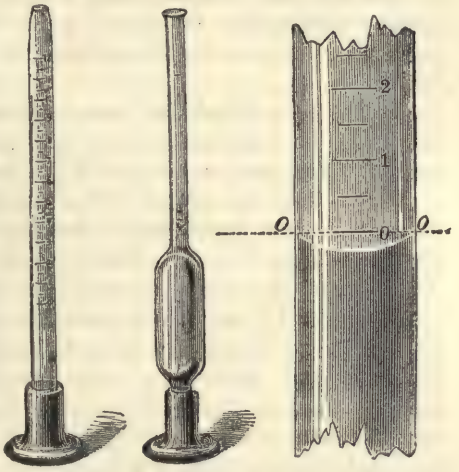
Acetometry.—Commercial vinegar varies greatly as regards the quantity of acetic acid it contains. The sp. gr. of a commercial vinegar is no certain indication of the quantity of acetic acid, owing to the fact that the vinegar nearly always contains foreign matters. The testing of the strength can therefore only be accurately effected by means of saturating it with an alkali. According to the ordinary method, first introduced for this purpose by Otto, ammonia is added to the vinegar to be tested until the previously added tincture of litmus becomes again blue; although this method is not absolutely correct—owing to the fact that the neutral alkaline acetates exhibit an alkaline reaction—this does not much impair the correctness of this process. Otto's acetometer is a glass tube sealed at one end, 36 centimetres long by 1·5 wide, whereon is engraved a double scale of divisions, one of these towards the bottom of the tube serving for measuring the vinegar coloured by litmus, while the upper scale is intended for measuring the test liquor. When it is intended to apply the test with this measuring tube, a certain quantity (indicated by the divided scale) of litmus tincture is first poured into the tube, next vinegar is added in sufficient quantity to fill the tube up to the second division; afterwards so much of the test-liquor is added as to restore again the blue colour of the litmus.

A very useful apparatus for determining the value of vinegar and essence of vinegar has been proposed by Hartmann and Hauer, of Hanover. A box contains a bottle of normal potassa-lye, a bottle of an indicator, a small pipette, a cylinder with a back of milk-glass (Fig. 382), and a mixing vessel for 50 and 80 per cent. essence of vinegar and glacial acetic acid at 100 per cent.

The method of using the apparatus is as follows:—The cylinder (Fig. 383) is twice well rinsed out with the vinegar to be tested, shaking it well, and expelling the last drops by a centrifugal movement. The sample is poured in until the surface of the liquid stands a little above the zero-point, and so much liquid is removed with the pipette that the top line, *o o* (Fig. 384) of the liquid, coincides with the zero mark. To this end, the pipette, which must be previously shaken out several times before use, is plunged with its point into the liquid. Its upper opening is then closed with the moistened fore-finger, and raised up until the point is just above the mouth of the cylinder. If too much liquid was taken out, so much is let flow back by gently raising the fore-finger until the zero-point is reached. When this is done, 2 drops of the

indicated liquid are added, and the normal lye is cautiously run in until the red clouds in the cylinder disappear more slowly. The lye is then added, drop by drop, until the vinegar is completely saturated. As soon as the entire liquid remains red, after careful agitation, the operation is at an end. The cylinder is set on a horizontal surface, let stand for a minute, and the degrees consumed are read off, which indicate how many per cents. of absolute acetic acid ($C_2H_4O_2$) are contained in.

Fig. 382. Fig. 383. Fig. 384



Testing Vinegar-Essence.—This may be effected on the principle just laid down.

Wood Vinegar.—After the dry distillation of wood a portion of the carbonised matter remains in the retorts as charcoal, while the remainder of the constituents of the wood are eliminated partly in the state of gases and vapours, such as carbonic oxide, carbonic acid, hydrogen, light and heavy carburetted hydrogens—partly in the shape of a condensed matter, consisting of a thick, brown, oily fluid floating upon a stratum of a watery liquor. The latter, wood vinegar, consists essentially of impure acetic acid, some propionic and butyric acids, small quantities of oxyphenic acid, creosote, and an alcoholic wood spirit, a mixture of methylic alcohol, aceton, and methyl acetate, the brown, thickish fluid substance known as wood tar, consisting of a number of both fluid and solid bodies, paraffin, napthalin, creosote, benzol, toluol, &c. A well-conducted distillation will yield as much as from 7 to 8 per cent. of the weight of the wood of acetic acid. According to the researches of H. Vohl, peat can be employed in the preparation of wood vinegar and of wood spirit. 10 cwts. of peat yield 3 kilos. of acetic acid and 1·45 kilos. of wood spirit.

Raw wood vinegar contains in solution a not inconsiderable quantity of resin, and also small quantities of phenol and guaiacol; all these bodies impart a more or less brown colour and empyreumatic odour and flavour, and they also render it a valuable antiseptic. Where the principal aim is to obtain wood vinegar, an iron retort, somewhat similar to a gas retort, is employed for the distillation of the wood. In large factories, instead of the wooden receivers, large stone or brickwork cisterns are employed, generally several of such tanks being used, the largest quantity of tar being condensed in the first cistern, while the wood vinegar, mechanically freed from the tar and floating on its surface, finds its way into a second cistern. Pettenkofer's patent wood-gas generators produce a not inconsiderable quantity of wood vinegar.

Purifying Wood Vinegar.—Raw wood vinegar is a clear dark brown fluid, having a tarry taste and smoky odour. It is employed in small quantities in the preservation of meat, also for the preservation of wood, ropes, &c.; but by far the largest quantity is employed in the manufacture of the various acetates used in dyeing and calico printing, chiefly as crude iron acetate and crude aluminium acetate. It is also used in the preparation of concentrated acetic acid for industrial purposes; that is, for the production of aniline from nitro-benzol, and of sugar of lead (lead acetate). Lastly, it is largely used in the preparation of table vinegar, an operation economical only where, as in England, there is a high duty on alcoholic fluids.

Among the means of purifying crude wood vinegar, the most simple—leaving out of the question the filtration of the crude liquor over coarsely granulated wood charcoal as recommended by E. Assmus—is distillation, an operation usually carried on in a still

made of copper fitted with a copper condensing apparatus. At first a yellow fluid comes over—raw wood spirit, from which the wood spirit of commerce is prepared—and next the distillate becomes richer in acetic acid.

The principal methods at present employed for the purification of wood vinegar may be considered as falling under either of two classes:—

a. The first includes the purifying of wood vinegar without saturation with a base; while

b. The second includes those methods in which the wood vinegar is purified by conversion into an acetate, the acetic acid being next separated by distillation with an acid possessing greater affinity for the base.

To the first class belongs Stoltze's method, consisting in first obtaining by distillation 10 per cent. of a liquid which is employed for the preparation of wood spirit; 80 per cent. of the liquid is next distilled off, and the empyreumatic substances contained are destroyed by the action of either ozone or chlorine. The purification of the crude wood vinegar by the second method is more generally in use among manufacturers, the inventor of the system being Mollerat. The crude wood vinegar is first saturated with lime, and the solution next precipitated with Glauber's salt to obtain sodium acetate; this salt is purified by crystallisation, and when in a dry state is so far heated that the empyreumatic matter it is mixed with becomes carbonised, and is thus rendered insoluble; the sodium acetate is then extracted with water, and the acetic acid separated from it by distilling the previously crystallised and dried salt with sulphuric acid. Instead of sodium acetate, the calcium acetate is frequently employed in the preparation of acetic acid from crude wood vinegar, the latter being saturated with lime, and the salt formed evaporated to dryness. The dry salt is roasted and treated similarly to the sodium acetate to calcine any empyreumatic products. The acid is employed in the distillation is, according to the method invented by C. Völckel, hydrochloric acid. The distillation can be effected in a retort with a helm of copper and a condenser of lead, tin, or silver. To 100 parts of acetate of lime 90 to 95 parts of hydrochloric acid at 1·16 sp. gr. are used. When hydrochloric acid is used in this preparation, instead of sulphuric acid, any contamination of the crude calcium acetate with empyreumatic or tarry matter does not affect the purity of the acetic acid which is obtained, provided the crude acetate be first so well dried as to be free from all other volatile substances; when sulphuric acid is used for this purpose, the result is that an acetic acid is obtained, which contains not only a large quantity of sulphurous acid, but also offensive volatile compounds, due to the decomposition (by the sulphuric acid) of empyreumatic resins and tarry matter present in the crude calcium acetate.

For the preparation of acetic anhydride 250 kilos. of sodium acetate, previously dried to a dust, are placed in a double kettle fitted with an agitator. The temperature in the kettle is raised to 140°, and a strong current of chloro-carbonic oxide is introduced. The oil which distills over must be carefully condensed, as it has a very irritating effect on the mucous membranes. The crude product (150 kilos.) is submitted to fractional distillation, and 100 kilos. of fairly true anhydride may thus be obtained. The temperature of 140° must not be exceeded, as otherwise acetose is formed in considerable quantities, and can scarcely be completely separated from the anhydride.

Formic Acid, $HCHO_2$, a natural secretion of ants [and many other insects, *e.g.*, larvæ of *Cerura vinula*, *Cychrus rostratus*, &c.] is obtained by heating oxalic acid with glycerine.

According to Lorin, we mix at 108° equal equivalents of oxalic acid and glycerine in small properties, allowing the escape of gas to come to an end after each addition. At first more water is liberated than corresponds to the carbon

dioxide evolved, and the water split off on etherification; the oxalic acid at first yields up simply its water of crystallisation. Subsequently the production of water and formic acid ceases almost entirely, though much carbon dioxide is still liberated, and ultimately the water which has escaped is exactly equal to the crystalline water and that formed by etherification, since about 91 per cent. of the formic acid are combined with glycerine. The same phenomena occur on further additions: the oxalic acid expels a part of the combined formic acid; the newly-formed formic acid escapes in part, and is partly taken up by the glycerine. At the third addition the glycerine is almost completely saturated, and 43 grammes of formic acid have been liberated. At the fourth addition there is formed from 1 equiv. of oxalic acid exactly 1 equiv. formic acid and the crystalline water. The synthetic production of formic acid by the action of moist carbon monoxide upon soda-lime at about 200° deserves attention.

Butyric acid, $H.C_4H_7O_2$, is obtained by the fermentation of a solution of sugar mixed with putrid cheese. Fitz dissolves 180 grammes sugar in 6 litres water, adds 0·1 gramme potassium phosphate, 0·02 magnesium sulphate, 1 gramme ammonium chloride, and 70 grammes calcium carbonate, heats to 110°, lets cool, and sows with a pure culture of *Bacillus butylicus*. He thus obtains 42 grammes pure butyric acid. Stinde recommends 50 kilos. carobs (*Ceratonia siliqua*) crushed up to a thin paste with water at 28°, adds after four or five days 12 kilos. of elutriated chalk, and lets the whole ferment, which in summer is completed in six weeks. The thick pasty mass is then etherified in a copper still by a mixture of 18 kilos. sulphuric acid and 30 kilos. alcohol at 95 per cent.

Butyric ether is used in perfumery as rum—or cognac ether.

Valerianic acid, $H.C_5H_9O_2$, is chiefly obtained by heating amylic alcohol with potassium dichromate and sulphuric acid. Its ethylic and amylic ethers are extensively used as *fruit ethers* (oil of apples).

Oxalic Acid, $H_2.C_2O_4$, a constituent of many plants (*oxalis*), is now almost exclusively obtained by melting sawdust with caustic potassa. Mixtures of potassa and soda give a smaller yield.

Thorn added 50 parts of sawdust to 100 parts hydrated alkali in the state of a lye of 98° Tw., and then heated it in a layer of 1 centimetre in thickness with frequent stirring. He obtained the following yields:—

Proportion of KHO to NaHO.	Temperature.	Oxalic acid.
		Per cent.
0–100	200°–220°	33·14
10–90	230°	58·36
20–80	240°–250°	74·76
30–70	240°–250°	76·77
40–60	240°–250°	80·57
60–40	240°–250°	80·08
80–20	245°	81·24
100–0	240°–250°	81·23

In experiments with different woods it was observed that soft woods proved to be the best material. On heating 50 parts of wood with 40 parts KOH and 60 NaOH, in thin layers, there was obtained:—

Kind of Wood.	Moisture.	Oxalic acid.	Oxalic acid calculated in wood dried at 100°.
	Per cent.	Per cent.	Per cent.
Pine . . .	15·0	80·5	94·70
Fir	15·0	80·5	94·70
Poplar . . .	14·0	80·1	93·14
Beech . . .	8·6	79·0	86·43
Oak. . . .	6·5	75·1	83·42

The melt is lixiviated with water, the solution is boiled with milk of lime, and the calcium oxalate is decomposed with sulphuric acid. If a mixture of soda and potassa is used for melting, the lye is concentrated to 66° Tw., when the sodium oxalate crystallises out and is freed from the mother liquor in a filter-press or a centrifugal. The sodium oxalate is dissolved in boiling water and the liquid is boiled with milk of lime for some hours. It is advantageous to use the solution very dilute, as otherwise the decomposition takes place very slowly. When a filtered specimen no longer gives the reaction of oxalic acid the lye is drawn off, the precipitate is washed with hot water and filtered. The lye is used again. An excess of sulphuric acid is required for the decomposition of the calcium oxalate, according to Chandelon, 3 mols. sulphuric acid to 1 mol. calcium oxalate. The salt is stirred up with water to a thin paste, and the requisite quantity of sulphuric acid (at 22° to 30° Tw.) is stirred in. It is then heated for some hours, after the addition of water, and filtered off from the calcium sulphate. The solution, which along with oxalic acid contains sulphuric acid and gypsum, is concentrated to 22° Tw. Gypsum separates out on standing, and after its removal the liquor is further concentrated to 50° Tw. On cooling, oxalic acid separates out in long crystals, and is purified by recrystallisation. The sulphuric acid can also be used again.

According to Merz, by quickly heating sodium formiate with the utmost possible exclusion of air to above 400°, a saline mass is formed, which contains along with carbonate 70 per cent. and more of oxalate. At lower temperatures more carbonate is formed. Potassium formiate behaves in a similar manner; calcium, barium, and magnesium formiates yield merely carbonates. It is, perhaps, possible that the synthetic formation of sodium formiate by means of carbon monoxide and its conversion into oxalate may prove a more advantageous method for the production of oxalic acid than the reaction of caustic potassa upon sawdust.*

Oxalic acid is used for bleaching straw, as a discharge in tissue printing, and in certain mordants used in woollen and silk dyeing. Its most important salts are the acid potassium and antimony oxalate, now used in tissue printing instead of tartar emetic.

Lactic Acid, $H.C_3H_5O_3$, is obtained by the fermentation of sugar with cheese, or preferably, according to Kiliani, by heating inverted sugar with soda lye. Antimony lactate serves as a mordant in dyeing in place of tartar-emetic.

Tartaric Acid, $H_2.C_4H_4O_6$.—Only the dextro-rotary tartaric acid is of technical importance. It is contained in grape juice and is deposited during fermentation as so-called tartar, or argol, which consists chiefly of potassium bitartrate. According to Kurtz, 500 to 700 kilos. of crude argol are heated to boiling in a wooden vat by the introduction of steam. Half the tartaric acid is then precipitated by the addition of powdered chalk. Less than the theoretical quantity of chalk must be used (18·8 potassium bitartrate require 5 parts of chalk), as the crude argol rarely contains more than 80 per cent. of acid potassium tartrate, and besides on complete neutralisation the magnesia, alumina, and iron oxide would be also precipitated. With tartars and argols, which are very rich in such impurities, it is advisable at the beginning of the operation to add 12 to 25 kilos. hydrochloric acid, and not to neutralise completely, as otherwise during the crystallisation of the tartaric acid the presence of alum, magnesium sulphate, &c., would cause much annoyance.

To convert the neutral potassium tartrate into the calcium salt, Kurtz recommends gypsum when cheaper than calcium chloride. 8·6 parts of gypsum equal 5 parts of chalk. The gypsum may be added before or during the neutralisation with chalk, and an excess does no harm. As the calcium tartrate obtained from the lyes is very pure, pure gypsum is used for working it up for potassium tartrate. The reaction of the calcium sulphate with neutral potassium tartrate is slow, and requires several hours.

* It was formerly obtained by the action of nitric acid on sugar.

As soon as acetic acid occasions no precipitate in a cooled and filtered specimen, the reaction is at an end. The contents of the vat are allowed to cool down to 50°, and are let off into another vat intended for the deposition of the calcium tartrate, passing through a sieve in order to keep back chips of wood, grape stalks, &c., usually present in crude argols. In three to four hours the calcium tartrate is deposited, and the lye is drawn off with a syphon. It is rich in potassium sulphate. When the lime salt has been washed three times it is sufficiently clear for further treatment.

In working up wine-lyes the alcohol present is first distilled off; then about 2500 kilos. are placed in a vat holding from 100 to 150 hectolitres, which is almost filled with water. About 50 kilos. of crude hydrochloric acid are added, and the whole is heated almost to boiling whilst stirring. The contents are then allowed to settle, and the clear liquid is drawn off through syphons into a second vat, in which it is nearly neutralised with powdered chalk whilst being constantly stirred. All the tartaric acid is precipitated by the calcium chloride which is formed. The liquid is drawn off into a third vat, where the calcium tartrate is deposited and washed. The muddy sediment of the first vat is pressed to recover any tartaric acid present, and the residue can be worked up for Frankfort black.

The process of Dieter has also proved successful. It consists in heating the crude tartar, or the dried, or the freshly pressed and liquid lyes, to 140°–170°, which is effected by steam at a pressure of 3 to 7 atmospheres, in closed pans; or by boiling under pressure, and by dry roasting with superheated steam. The impure product is easily lixiviated, and the tartaric acid solution is separated out by means of filter-presses.

The calcium tartrate is decomposed by sulphuric acid. More than the theoretical quantity of sulphuric acid must be used (which would be 4·9 parts to 9·4 calcium tartrate), as fine crystals of tartaric acid can be obtained only from solutions containing strong mineral acids. The presence of small quantities of calcium tartrate or potassium sulphate (resulting from imperfect washing of the calcium tartrate) greatly disturbs the crystallisation. The lime-salt is mixed with the sulphuric acid, the needful amount of water is added to obtain a paste which admits of stirring, and it is heated by means of steam to 75° with agitation. As soon as the sulphuric acid is in a certain excess (which is judged by the bulk of the precipitate produced by a filtered specimen with calcium chloride), the tartaric acid is separated from the gypsum by filtration, and is boiled down in leaden pans by means of a steam worm of lead, when a little gypsum separates out. As the lye becomes more concentrated the heat must not be allowed to exceed 70°–75°, as otherwise the tartaric acid will be turned brown by the sulphuric acid. At the concentration of 72° Tw. the lye is run into wooden tanks lined with lead, or large earthenware pans, and allowed to crystallise. The mother liquors are evaporated down three times, taking each time a crop of crystals. The fourth mother liquor is treated as a raw material. The crystals are whizzed,* redissolved, and decolorised with bone-black; the solution is filtered, mixed with a little sulphuric acid, evaporated down to 72° Tw., and again run into the crystallisers. The acid, which is now finely crystallised, is whizzed and dried.

In some works the evaporation of the tartaric solutions is very successfully carried on in lead vacuum pans.

The yearly production of tartaric acid is, in hectokilos.:

Germany	8000
Austria-Hungary	5000
France	3000
Italy	2000
Spain	500
Britain	13,000
United States	12,000

amounting in value to 16–20 million marks.

* The ordinary technical expression for treatment in a centrifugal machine.

Tartaric acid is used in large quantities as a discharge in tissue printing, as a mordant in dyeing (in the state of acid potassium tartrate), in the preparation of baking-powders, effervescing drinks, &c.

Citric Acid, $H_3.C_6H_5O_7$, is especially present in the juice of lemons and limes (6 to 7 per cent.), and of currants. To obtain it, limejuice is precipitated with milk of lime, the calcium citrate is decomposed with sulphuric acid, and the solution of citric acid is evaporated down. Citric acid is used as a discharge in tissue printing and in the manufacture of lemonades.

Benzoic Acid, $H.C_7H_5O_2$, is prepared for medicinal uses from the gum-resin benzoin. For technical purposes it is obtained from hippuric acid or from naphthalene or toluene. In its preparation from hippuric acid, which on boiling with dilute acids or on putrefaction is split up into benzoic acid and glycocol, the urine of horses or cows is either boiled for a long time with hydrochloric acid or it is allowed to putrefy, precipitated with milk of lime, filtered, the filtrate is concentrated, and the benzoic acid is thrown down by hydrochloric acid. For purification it is dissolved in weak milk of lime with a little chloride of lime, reprecipitated by hydrochloric acid and recrystallised. The acid thus obtained has a slightly urinous odour.

For obtaining benzoic acid from the phthalic acid produced by the oxidation of naphthalene, its calcium salt is heated to 330°–350° :

$$2CaC_8H_4O_4 + Ca(OH)_2 = Ca(C_7H_5O_2)_2 + 2CaCO_3.$$

According to Laurent, the ammonium compound of phthalic acid by dry distillation is converted into phthalimide, and this again by distillation with slaked lime into benzonitril :

$$C_8H_5O_2N + Ca(OH)_2 = C_7H_5N + 2CaCO_3 + H_2O.$$

On boiling with caustic soda lye, benzonitril is converted into sodium benzoate, whilst ammonia is liberated :

$$C_7H_5N + NaHO + H_2O = NaC_7H_5O_2 + NH_3.$$

Sodium Benzoate.—Toluene is converted into benzylchloride, C_7H_7Cl, by treatment with chlorine, and this compound, if heated with water under pressure or boiled with dilute nitric acid, passes into benzoic acid. G. Lunge boils 100 parts benzylchloride with 300 parts nitric acid at 60° Tw. and 200 parts of water for ten hours, with a reflux condenser. Benzoic acid melts at 121° and boils at 249°.

Tannin, $C_{14}H_{10}O_9$, is found chiefly in nut-galls and also in sumac. It is obtained by extracting powdered nut-galls with ether. A mixture commonly employed consists of 30 parts ether, 4 parts water, and 1 part alcohol. The acid obtained by evaporation may be purified from the accompanying gallic acid by solution in lime and precipitation with solid sodium chloride, or by repeated solution in water and treatment with animal charcoa

Tannin serves for clarifying wines (rarely beers), but chiefly as a mordant in dyeing, for the production of ink and of pyrogallol, and in medicine.

TREATMENT OF COAL-TAR.

The so-called aromatic compounds are almost entirely obtained from coal-tar. Most tar is obtained in the manufacture of coal-gas, and a smaller quantity from coke-burning. The composition of the tar depends on the quality of the coal, but still more on the temperature employed.

According to Wright, the specific gravity of tar is the higher the stronger the heat which has been employed. Five tars obtained from the same coals, but at an increasing temperature, yielded :

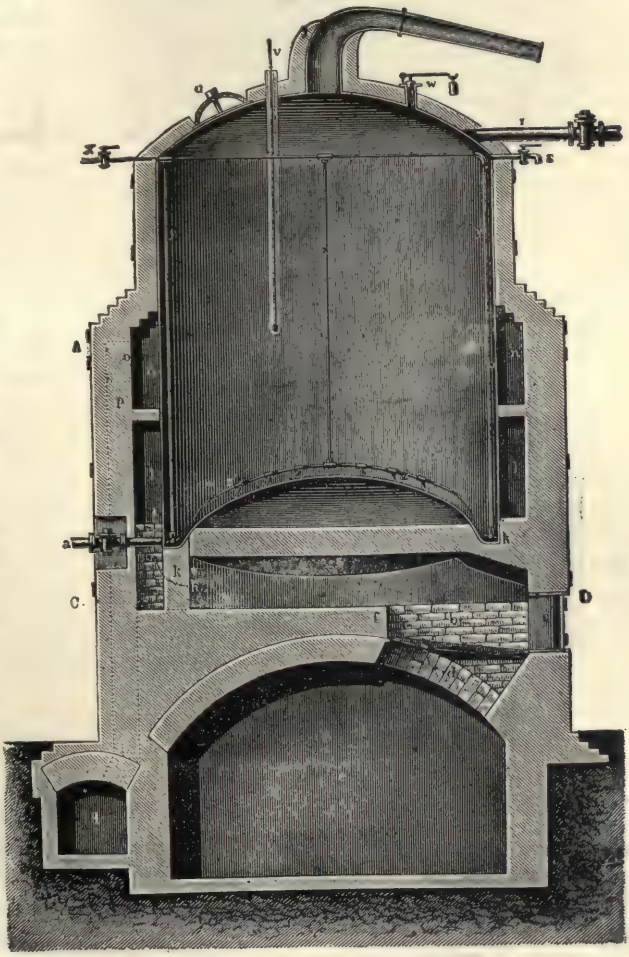
	I.	II.	III.	IV.	V.
Specific gravity of tar . .	1·086	1·102	1·140	1·154	1·206
Ammonia liquor . . .	1·20	1·03	1·04	1·05	0·38
Crude naphtha . . .	9·17	9·05	3·73	3·45	0·99
Light oils	10·50	7·46	4·47	2·59	0·57
Creosote oils	26·45	25·83	27·29	27·33	19·44
Anthracene oils . . .	20·32	15·57	18·13	13·77	12·28
Pitch	28·89	36·80	41·80	47·67	64·08

The quantity of crude naphtha (benzol, &c.) of the light oils and the phenols decreases rapidly with the rise of temperature. Tar from the Berlin gasworks contains in 100 parts :

Benzol and Toluol	0·8
Other clear oils	0·6
Phenol	0·2
Naphthaline	3·7
Anthracene (pure)	0·2
Heavy oils	24·0
Pitch for asphalt and briquettes, &c. . .	55·0

For the distillation of tar, Lunge recommends the still intended for 25 tons of tar, of which Fig. 385 shows the section, on the line *E F* of the ground-plan; Fig. 386 a section through *D C'* of Fig. 385; Fig. 387 a section through the body of the still itself along *A B* of Fig. 385. The body is 3 metres in width and $3\frac{1}{2}$ metres high without the capital, and is constructed of boiler-plates 10 mm. in thickness. A concavity of the bottom corresponds approximately to the convexity of the cover. The body may have a very slight slope towards the side of the outflow cock, *a*, which, however, must be placed as close as possible to the bottom or even in its flat part.

Fig. 385.



The fire-box, *b*, is accessible from without by the door, *c*, which must be placed on the side opposite to the exit-cock for the pitch. In the drawing is shown the arrangement of one of the largest English manufactories, in which the wall underneath the fire-doors is closed in front, and the ashpits are all connected through the opening, *d*, with a large vaulted channel, *e*,

which runs underneath the entire series of stills, and which is accessible only at both ends. This affords complete security against the danger of fire, in case the tar in the stills should boil over, fill the receivers, and flow away from the latter.

The flame strikes over the fire-bridge, *f*, and beneath the vault, *g*. The latter is struck as a tun-vault from the circular wall, *k*, upon which the still rests, and completely protects its bottom from the pointed flame. The space between *g* and the bottom of the still is merely an air-bath, the temperature of which is kept high by the flame playing underneath *g*, but can never become excessive. In *g* so much heat is stored up that towards the end of the distillation there is no need to fire up. The weight of the still-body, resting upon the ring-wall, *k*, makes the latter a safe bed for the protective vault, which is quite independent of the masonry of the fire-box, and can be repaired without interfering with the work. The flame passes through the four flues, *h*, into two vertical channels, *i*, to arrive at the cylindrical jacket-wall of the still. The massive pillar, *i'*, between the channels, *i*, is continued some distance above. In it there lies, protected from the fire, but kept warm by the channels, *i* and *p*, running close alongside, the pipe which connects the exit-cock with the body of the still. The pillar, *i''*, compels the flame to divide into a left and a right stream, which pass round the lowest part of the still-body in the ring-channels, *l*, are hindered from uniting in front by the pillar *i''*, pass through the flues, *m*, into the upper ring-channel, *n*, pass again backwards, and open through *o* into the perpendicular shafts, *p*, which are connected with the main smoke-flue, *q*. The shafts, *p*, are interrupted at suitable places by slides, by means of which a uniform heat can be kept up on both sides of the still-body. Above the fire flues the body is protected against the radiant heat with a wall, 0·22 metre in thickness; this is carried up above the cover, and preferably above the ascending part, *t*, of the capital. A protection of this kind is the more necessary when, as it is to be recommended, the stills are quite in the open air, or merely covered with a slight roof of corrugated iron. Any explosions or fires are then much less destructive than when

Fig. 386.

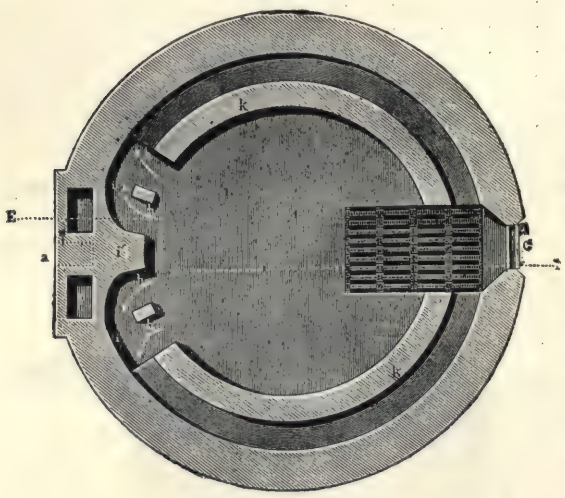
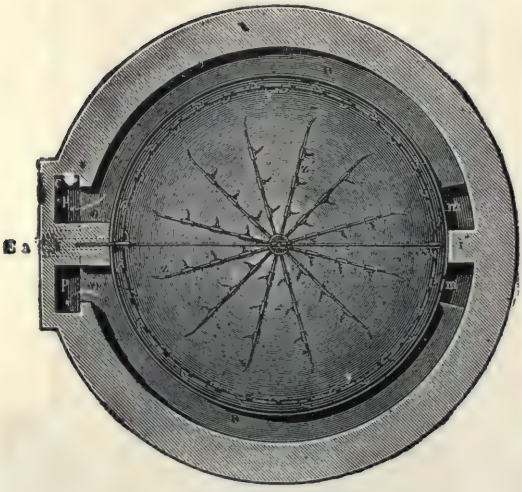


Fig. 387



the stills are fixed in a massive building. When the stills are uncovered, the masonry should be coated with melted pitch as a protection against the rain.

The charging is effected by means of the cast-iron pipe, *r*, closed with a slide cock or otherwise, and about 0·15 metre in width, so as not to take too much time in filling the still. If the tar is not pumped in, but let flow down from a tank at a higher level, there is provided a filling-hole, which is afterwards closed with a conical iron plug or a screw. There is also an air-hole through which the height of the liquid can be gauged; preferable to both is an overflow cock, *s*, of 25 millimetres in width. Through this there escapes at first air; if tar flows the feeding is stopped and *s* is closed.

The vapours are led through the cast iron capital, *t*, which tapers from 0·3 to 0·15 metre, and is then prolonged into an iron-pipe of the same width, leading to the cooler. Sometimes there is placed at the base of the capital in the inside a channel which leads the liquids condensing in the ascending part of the capital direct to the outside, so that they may not drop back into the still, and occasion frothing. This arrangement is scarcely necessary if the ascending part of the capital is covered with poor conductors of heat. Sometimes a steam-pipe is made to open into the capital to remove any obstruction. But with a capital of the above width and with a slight fall such stoppages cannot happen.

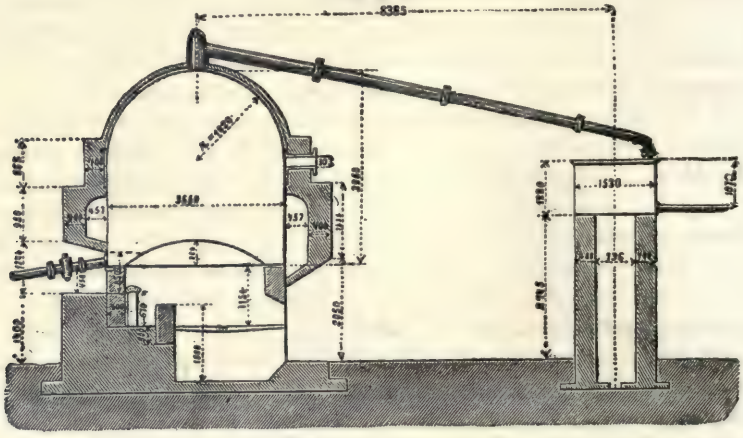
Each still has a man-hole. This is shown at *u*, as in a steam boiler, and is closed by a lid pressed down by a screw handle. It is tightened either by a border of fatty clay or a ring of asbestos paper. In some places the cover of the man-hole acts as a safety-valve. It consists then of an iron plate lying loosely upon a corresponding short tube, the connecting joints being connected with some cement which does not set too hard. If the pressure in the still rises too high the cover of the man-hole is thrown off before injury can be done. In default of such an arrangement a real safety valve should be provided, as is here shown at *w*, though many stills are left without such an arrangement. It is very convenient to attach a lateral pipe leading away from the capital, with a safety valve opening downwards, so that in case of boiling over the tar may be led to a place protected from fire. The insertion of a thermometer, *v*, is to be recommended. It is inclosed in an iron tube filled with iron filings and mercury and reaching down to half the depth of the still.

In the figure there is seen a system of tubes, *x y z*, for introducing steam into the still. This is generally effected merely by cross tubes with apertures in their arms for the escape of the steam. Here the full arrangement is shown as designed by Trewly and Fenner. The steam is led in by a pipe 25 millimeteres in width, with a cock, *x*, which gives off in the inside three descending pipes, *y z y*. Of these *y* is connected with the ring-tube, *y'*, which lies at the lowest part of the still, and *z* is in connection with a system of branch tubes, *z*, which cover the entire bottom of the still. Both from *y'* and from *z'* there branch off a great number of open, slightly curved exit tubes with tapering mouths. The steam streaming in through this apparatus is divided into very many slender jets, which sweep over all parts of the still-bottom, prevent it from being overheated, and carry along the vapours of the heavy hydrocarbons. In consequence of the great surface of the distribution tubes the steam becomes superheated before escaping, and there is no need for a special superheater.

Another still, for a charge of 25 tons, has the dimensions given in Fig. 388. The vaulted bottom is rivetted together out of 12 plates fixed star-shaped, which are united at their inner ends by a round plate. A German establishment has larger stills, of 4 metres diameter and 4 metres in height from the lower angle of the bottom to the upper angle of the cover, and are fitted for the distillation of 35 tons of tar. The bottom of the still either lies in the open fire or is protected by a grating, which is always to be recommended where thick tars are worked, which readily form a deposit of coke on the bottom and allow the plates to become red hot. The cooling

worms have an inside width of at least 13 centimetres and an incline of 2 per cent. in a length of 48 metres. The trough for receiving the cooling worm is $5\frac{1}{2}$ metres long, 1·53 metre wide, and 1·23 metre deep. The longitudinal tubes lie 1·10 metre apart, measured from middle to middle, and the cross tubes are 4·76 metres apart, so that the total surface traversed by the tar is about 20 square metres, whilst the largest section of

Fig. 388.



the still is $10\frac{1}{2}$ square metres. The cooling worm is of wrought iron, and only that part which stands up out of the water and is connected with the beak of the still is of cast-iron, as a wrought iron piece is very quickly destroyed at the point where the surfaces of air and water come in contact. In order to keep the cooling-worm clean, a steam pipe is attached at the point where the beak and the worm meet, and steam is blown in in case napthaline begins to be deposited. But if this crystallisation of napthaline in the cooling-worm has made too much progress the cooling-water has to be heated by blowing in steam, so as to melt the deposit and open the way of issue for the distillate.

The stills are filled either by means of a pump or a montejus, in both of which cases the error of having too narrow tubes must be avoided. For tar the pipes should never be below 130 millimetres inside diameter, and for creosote and anthracene oils not less than 80. In filling the still with tar the inflow-pipe must project with its mouth beyond the side of the still, thus preventing the tar from running down the sides, as the plates at this spot are quickly corroded by the sulphur-compounds of the ammonia-water and the tar. Many tars are characterised by an abnormal proportion of carbon, which on distilling attaches itself to the bottom, and sometimes produces a considerable deposit of coke, even after a single operation, so that the distillation cannot be completed without considerable danger. It is hence advisable, before purchasing, to distil not merely a small quantity of the tar, but to shake out and wash a small average sample with benzol, and to dry and weigh the residue. 42 Westphalian, Rhenish, and North German tars gave proportions of carbon from 7 to 33 per cent. The latter percentage was found in the tar of a large, well-arranged gas works on the Rhine, which had in consequence great difficulty in the disposal of its tar. In order to distil such tars without injury to the still bottom this carbon should be kept in suspension either by blowing in super-heated steam, or by means of an agitator. By means of the latter expedient it was found possible to effect 15 distillations, each of 25 tons in succession, and to interrupt the work then merely to ascertain the general state of the still. The bottoms, even after such a number of operations, were almost free from coke, and since the introduction of the agitators the consumption of coal had considerably diminished. The only disadvantage lay in the polishing off the rivet-heads in the

bottom, and wearing out the chains of the agitator, so that after six months it was necessary to re-rivet the bottom and to renew the chain. The bottoms of the stills were uninjured, although they had no protective vaults, and the wearing of the rivet-heads is avoided if they are counter-sunk. It was only possible to distil highly carboniferous tars by means of agitators, and to work upon hard pitch, which was softened by the addition of tar-oils of low value.

The cooler for pitch is best made of masonry, and not of iron, as the latter material cools too unequally, and renders a frequent cleansing of the cooler needful. After cleaning out with a pick-axe it is recommended to admit steam as dry as possible.

The distillation must be conducted very cautiously at first, as the tar is apt to boil over as long as any ammonia water is present. According to the indications of the thermometer in the still the following fractions are separated:

1. First runnings . . . up to 105 or 110°
2. Light oils up to 210°
3. Carbolic oils (for phenol and naphthaline), up to 240°
4. Heavy oils up to 270°
5. Anthracene oils above 270°

Towards the end of the distillation the condensing water must be kept warm to prevent the distillate from solidfying in the cooling pipes and causing an obstruction. Steam is often introduced into the still for the same reason, sometimes being previously super-heated. Lunge obtained as an average:

First runnings	2·4 to 3·5 per cent.
Light oils	6·0 to 6·7 „
Heavy oils	30·4 „
Hard pitch	55·0 „

According to Häussermann a tar of German origin gave:

Fractions.

Light oil	5·0 to 8·0 per cent.
Heavy oil	25·0 to 30·0 „
Anthracene oils	8·0 to 10·0 „
Pitch	50·0 to 55·0 „

Final Products.

Benzol	0·6 per cent.
Toluol	0·4 „
Higher homologues	0·5 „
Pure naphthaline	8·0 to 12·0 „
Phenol	5·0 to 6·0 „
Anthracene	0·25 to 0·3 „

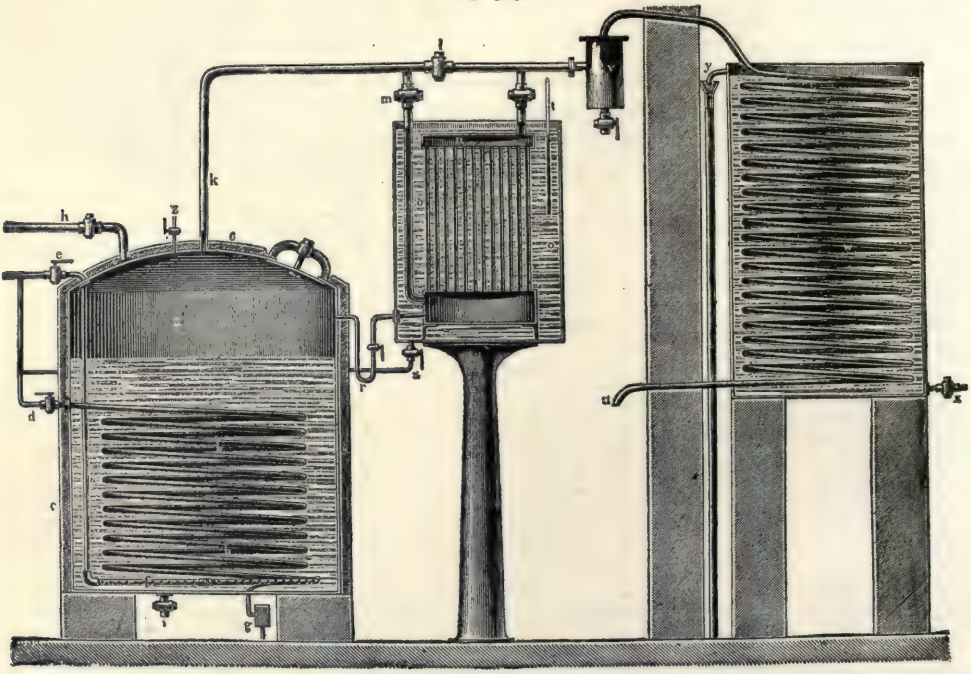
The value of the pitch depends on its proportion of oils, determined by dissolving the sample in benzol, filtering, washing the residue (in benzol), and evaporating the benzol, when the weight of the carbon present is ascertained at the same time. Another method, chiefly followed at briquette works, for determining the quality of soft pitch, consists in keeping a fragment of the sample of about 100 millimetres in length and 10 millimetres in thickness, in hot water at 60° for two minutes. The piece must admit of being bent without cracking. For harder sorts a temperature of 70° is used. It serves for the manufacture of "coal-blocks," as an addition to asphalt, to lacquers, for roofing, papers, &c.

The treatment of the heavy oil for naphthaline is generally not remunerative. It is therefore used for saturating wood, for softening hard pitch, as a tar varnish, for producing blacking, for lighting, or it is burnt like tar. The light oil, the carbolic oil, and the anthracene oil, are worked up specially.

The *light oil* (crude naphtha) is first treated with strong sulphuric acid, and then with soda-lye, in order to remove the pyrogenous resins, olefines, &c. Lunge mixes 100 kilos. of naphtha with 12 kilos. sulphuric acid for ten to fifteen minutes, and lets the mixture settle over night. The naphtha is then separated from the acid (the utilisation of which has not yet been effected), washed repeatedly with water, treated with soda-lye of sp. gr. 1·1, washed again, and then distilled. The crude benzol obtained up to 110° is farther purified.

According to Lunge, Fig. 389 shows an apparatus used in English manufactories. The still, *a*, is heated by the steam-pipe, *d*, which is continued in a spiral, *b*, of lead or wrought-iron, with the pipe, *g*, for carrying off the condensed water. The direct introduction of steam is effected by the cock, *e*, and the cross of perforated tubes, *f*; *h* is the feed-pipe, *i* the outlet-cock, *k* the capital. In order to carry away the steam the cock, *l*, is opened, and the steam rushes first into the spirit-catcher, *v* (which should never

Fig. 389.



be wanting), and into the cooling-pipe, *w*, a lead tube of 35 mm. inside diameter, the end of which, at *u*, returns into the space where the receivers are placed. The cooling-vat is fed at *x* with cold water, which runs off hot at *y*. But if the vapours are to be purified, the cock, *l*, is closed and *m* is opened. The vapours then pass into the condenser, *n*, the lower drum of which is connected with the upper by about fifty copper tubes only 10 mm. wide. The condensed oil runs through the hydraulic joint, *r*, back into the still.

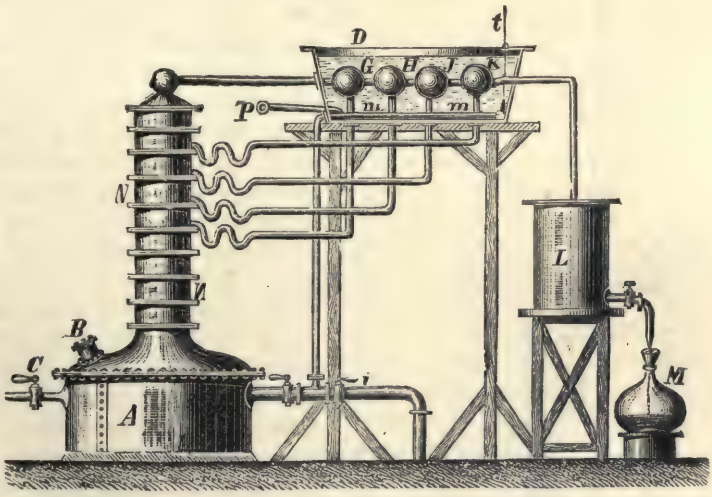
Heat is applied at first by the closed steam-pipe, *b*, and afterwards by the introduction of steam through the pipe, *f*. In order to separate the benzol, which passes over first as free as possible from toluol, the vapours arriving through *h* are compelled to flow into *n* by closing the cock, *l*, and opening *m*, whilst the water of *o* is heated to a sufficient temperature by means of the steam-cock, *s*. For so-called 90-per cent. benzol the water is kept at 60°, for 50-per cent. benzol at 70° or 80°; but these numbers cannot be absolutely fixed, and must be determined for every apparatus. The

temperature in *o* is kept as constant as possible. What condenses in *n* flows back through *r* to the still *a*; it is chiefly toluol, containing little benzol. What is not liquified in *m*—*i.e.*, vapours of benzol containing little toluol—passes into the main steam-pipe, thence into the cooling-worm, *w*, and the benzol condensed there flows through *u* into the receiver.

After some time scarcely anything comes from *u*, and now, in order to obtain weaker benzoles, the temperature in *o* must be raised. In general, even if it is desired to produce pure toluol, it is possible to work with water in *o*, which, however, must be heated to a boil. Water can the more readily be used if the intention is to obtain benzol at 30 or 40 per cent., as is generally the case. In most distilleries it is not sought to effect any further separation into pure hydrocarbons, and hence purification is not carried any further. If nothing more runs from the worm, *w*, the condenser, *n*, is thrown out of action by closing the cock, *m*, and opening *l*. All the vapours pass now directly to *w*, and are there condensed, so that there is again an abundant distillate. By degrees this again grows less, and when little or nothing more is obtained the indirect steam from *e* is shut off, and by opening *d*, direct, steam is allowed to issue from the apertures of the cross-tube, *f*, and we have then, even with steam of only $2\frac{1}{2}$ to 3 atmospheres, a plentiful distillation of xyloles and trimethyl benzoles, which mixtures are either used as solvent naphtha and burning naphtha, or are further worked up for xylol, &c.

The distillation-apparatus of Coupier, very extensively employed, consists (Fig. 390) of the body, *B*, into which are introduced the benzoles to be submitted to fractional distillation. The still is heated by steam admitted by the pipe, *C*. The vapours given off from the boiling liquid arrive in the column, *N*, which acts as a dephlegmater, where the first fractionation occurs. The most volatile constituents of the vapours, not condensed in *N*, arrive in the apparatus, *D*, filled with solution of calcium chloride, which is raised by the steam-pipe, *m*, to a certain temperature, ascertained by the thermometer, *t*. The steam of the heating-pipe escapes through *P*. If pure benzol (benzene) is to be obtained, the solution of calcium chloride is heated to 80°. The vapours arriving at *G* are a mixture of benzol, toluol, &c. As the temperature of *G* is not above 80°, the vapours of toluol or other homologues, such as xylol, condense there, whilst the vapours not condensable in *G* pass on to the recipients *H*, *J*, *K*, depositing there the last traces of the less volatile hydrocarbons, and are finally condensed in the refrigerator, *L* (fed with cold water), and are received in the flask, *M*. The liquids condensed in *G*, *H*, *J*, and *K* pass back into the column, *N*. As the receiver, *G*, contains the heaviest products, they must be conveyed to the lowest part of *N*, whilst the

Fig. 390.



products of condensation from *K* are passed into the upper part of the column. If it be desired to obtain, not benzol but toluol, the temperature of the calcium chloride apparatus must be raised to 108° to 109°.

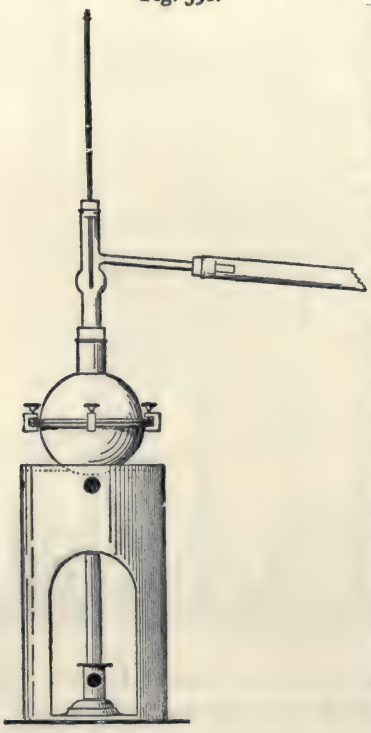
For obtaining pure benzene a column apparatus is used, such as is employed in rectifying spirits.

In English commerce the following ultimate products of the light oils and the first runnings are distinguished, to which Lunge (according to his own analysis of the products which he has himself obtained), appends the results of fractionation in volume percentages :—

Commercial names.	Boils at	88°	93°	100°	110°	120°	130°	138°	149°	160°	171°
90 p.c. Benzol .	82°	30	65	90	—	—	—	—	—	—	—
50 p.c. Benzol .	88°	—	13	54	74	90	—	—	—	—	—
Toluol . .	100°	—	—	—	56	90	—	—	—	—	—
Carbonating naphtha .	108°	—	—	—	1	35	71	84	97	—	—
Solvent naphtha.	110°	—	—	—	—	17	57	71	90	—	—
Lamp naphtha .	138°	—	—	—	—	—	—	—	30	71·5	89

Bannow's boiling vessel (Fig. 391) for determining the boiling point of benzol consists of a globular body holding 200 c.c. and made of sheet platinum, silver, or copper of 0·7 mm. in thickness. The diameter is about 73 mm. The body consists of two parts, which are held together by four screw clamps, the joint being made good with a washer of pasteboard, slightly moistened or oiled, 1 mm. in thickness. The upper part carries a short piece 25 mm. in length and 20 in width to receive the boiling tube. The glass boiling-tube of 12 to 14 mm. outside diameter and 100 mm. in length is expanded globularly in the middle; the side-piece is melted on at about 10 mm. above the globe, almost at right angles, and so as not to encroach upon the clear internal width of the tube. The body stands upon a plate of asbestos, with a circular aperture of 30 mm. in diameter; the stove is provided at 10 mm. from its top edge with four round openings for letting out the products of combustion. The source of heat is a plain Bunsen burner with an aperture of 7 mm. in diameter; the flame must burn a pure blue at every position of the cock. The Liebig's condenser to be used is $\frac{8}{10}$ metre in length, and is inclined so that the outflow is 100 mm. lower than the influx. The thermometer has a scale which can be displaced by a screw, and must be made of thin glass; the outside diameter must not be more than half the inside diameter of the boiling tube. It is so placed that the bulb shall be in the middle of the globe of the boiling tube. The charge consists of 110 c.c.; the first 3 c.c. passing over are to be rejected. The distillation is so regulated that 5 c.c. pass over per minute (2 drops per second); it is continued until the graduated receiver is filled up to the mark—100 c.c. A correction for the height of the barometer is not applied, but before every experiment the thermometer is adjusted to the boiling point of a standard specimen by means of the movable scale. This is

Fig. 391.



done at the moment when 60 c.c. of the 100 c.c. of the type specimen have distilled over.

On shaking up with sulphuric acid of sp. gr. 1·845 the benzol must not be discoloured at all and the acid not immediately. In ten minutes it may turn slightly yellow. If poured into nitric acid at 72° Tw. no white vapours must be produced, and on shaking the benzol must not be coloured. On prolonged standing the nitric acid turns slightly reddish; afterwards it becomes colourless and the redness passes to the benzol.

Benzene.—The pure substance C_6H_6 boils at 80° and solidifies at 0°; sp. gr. at 0° = 0·8991; at 15° = 0·8841. It is slightly soluble in water, easily soluble in alcohol, ether and methyl-alcohol. Common coal-tar benzol contains generally thiophene, C_4H_4S, and carbon disulphide.

Toluol (called toluene when absolutely pure) a benzyl-benzol C_7H_8 or $C_6H_5.CH_3$, boils at 110°; its sp. gr. at 15° = 0·872. It is also obtained from wood-tar.

Xylol or dimethyl-benzol from coal tar $C_8H_{10} = C_6H_4(CH_3)_2$ boils at 138° to 140°.

The *light oil*, containing some benzol, much toluol and its higher homologues, phenoles, naphthaline and liquid oils is rectified. The fraction up to 120° is added to the corresponding fraction of the first runnings (of the main distillate up to 150°). The fraction from 150° to 190° is purified with acid and alkaline lye, and is then taken to a second rectification. The residue (above 190°) goes to the heavy oils. The second rectification of the chemically purified fraction 120° to 190° gives:—

(*a*) Product up to 120° contains benzol and toluol, and comes to the corresponding product from the first runnings.

(*b*) Product from 120° to 127° gives benzene No. 1. for taking out spots.

(*c*) Product from 127° to 140° gives benzene No. 2.

(*d*) Product from 140° to 150° gives benzene No. 3.

(*e*) Residue comes to the heavy oil.

For obtaining phenol it is advantageous not to work up all the light oil, but to take the portion which passes over last, the so-called carbol-oil, which has in general the sp. gr. 0·99 to 1·005. It is treated with soda lye, which dissolves the phenoles, (tar-acids), whilst the oil not soluble in soda is worked up for naphthaline. The solution of sodium carbolate is decomposed by the addition of sulphuric acid, or, better, by passing into it carbonic acid.

The *crude carbolic acid* thus obtained contains only about 50 per cent. phenol with water, creosotes, naphthaline, &c. It is purified by redistillation, and the part passing over between 175° to 200° is set in a cool place to crystallise. Or the crude carbolic acid is treated with 1 per cent. potassium dichromate and the quantity of sulphuric acid at 1·845 sp. gr. necessary for its decomposition, stirring constantly. This is done in a flat vessel, so that the carbolic acid may present the greatest possible surface to the air; the sulphuric acid is added first, and then the solution of the dichromate, and the whole is stirred for some hours, being placed if possible in a place exposed to the sun. The contents of the flat pan are then drawn off into a deep glass jar, allowed to settle, and the oil is drawn off and distilled between 170° to 198°, whilst the first runnings of this distillation are added to the next distillation of crude oil, and the residue in the still is again distilled with the crude tar. The fraction passing over between 170° and 198° is again treated in a flat vessel with 1 per cent. potassium dichromate, and a corresponding quantity of strong sulphuric acid, stirred for some hours, drawn off from the dregs and distilled in a small column apparatus. The distillate is collected in small half-litre bottles until the contents of the still begin to become thick, which is found by stirring with an iron rod. The bottles are at once well closed, and let stand to crystallise, the oil is poured off from the crystals, which are melted in the water bath, and collected in dry ½ litre glass bottles.

Phenol (carbolic acid), C_6H_5OH, melts at 42° and boils at 182°. It dissolves in 20 parts of water, but at any proportion in alcohol, ether and benzene. Phenol is poisonous, but it is a good disinfectant. The cause of its turning red has not been ascertained with certainty.

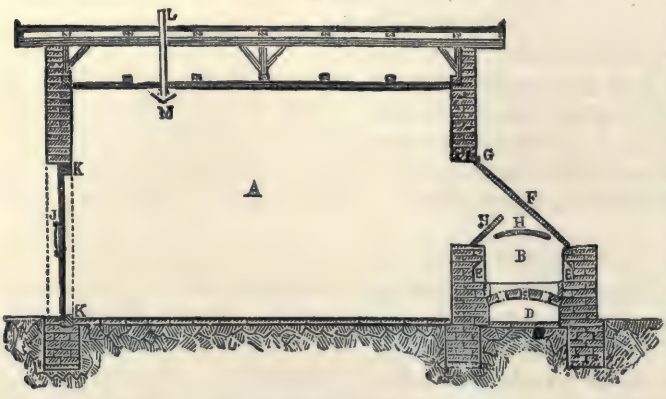
The quantitative determination of phenol is effected volumetrically with bromine. It is used in preparing colours, explosives (picrates) and as a disinfectant.

Cresol, or the cresylic acid of coal-tar, C_7H_8O or $C_6H_4.CH_3OH$, boils at 190° to 203°, and is a variable mixture of metacresol, orthocresol, and paracresol.

The oil drawn off from sodium carbolate is first re-distilled, and then set in a cold place, the naphthaline which crystallises out is pressed and once more distilled. This distilled naphthaline, in order to remove the pyrogenous resins, is melted in a double iron pan lined with lead, along with 1 per cent. of sulphuric acid at 156° Tw., and stirred for some hours. After prolonged settling, the sulphuric acid is separated from the naphthaline and the latter is sublimed in an upright still over an open fire. Into the naphthaline there opens a pipe for the direct admission of steam, and in the capital of the still a pipe which introduces steam from a fine aperture. As soon as the thermometer plunging into the naphthaline marks 160°, dry steam is let in very gently from both pipes. The beak of the still opens into the sublimation building, consisting of an antechamber and a main chamber 12 metres long, 3 metres high, and 2 metres in breadth. The liquid naphthaline passing over collects in the antechamber, which is 3 metres in length.

According to another communication there is used a subliming chamber, A (Fig. 392), 5 metres long and 3 metres wide. The wrought-iron pan, B, 3 metres long and 1 metre broad, is built in so over the grated arch, C, that the fire-gases from the heating-room pass backwards through D, below the grated arch, rise up in the flues, E E, leading round the subliming pan, B, and escape at the chimney. The door, F, which turns on an axle, G, is luted up with clay during the sublimation. Two wooden covers, H, coated with sheet-iron placed above the pan, rest upon iron clasps which are secured in the two side walls, cutting off the door, F. These two doors act like the dephlegmators in distillation, as vapours of the heavier, less volatile tar oils, carried along by the vapours of the naphthaline condense here on their surfaces and flow back into the pan. The wooden door, J, also lined with sheet-iron, can be removed on cleaning the naphthaline out of the chamber. To the iron air-pipe, L, 8 centimetres in thickness, there hangs the dish, M, which serves to catch the water condensed in the air-pipe. The pan is filled with crude naphthaline and from 3 to 4 per cent. of slaked lime is added; the doors are then luted up with clay, and at first a strong fire is kept up, but as soon as the sublimation begins it is kept very slight and uniform. In the door, F, there is a small hole so that the depth and the quality of the naphthaline remaining in the pan can be tested with an iron rod. The hole, of course, is closed with a cork. In two-and-a-half to three days, if the heat has been maintained all day, the pan will be empty down to 6 to 8 centimetres. It is

Fig. 392.



now frequently tested with the iron rod, and when it is seen that the naphthaline no longer congeals upon the iron the heating is stopped, because merely heavy tar oils remain in the pan. The pan is then emptied, charged afresh, and the sublimation is continued. When two or three pans have thus been worked off the sublimed naphthaline is cleared out of the chamber. It is melted in an open cast-iron pan with an emptying spout, and mixed with a 20 per cent. lye at 27° Tw., the lye is let off and there is added to the liquid naphthaline 6 per cent. of sulphuric acid at 156° Tw., and a little pyrolusite. After stirring diligently for fifteen or thirty minutes, according to the size of the pan, the naphthaline is allowed to settle, and in an hour the acid is drawn off. The naphthaline is then twice washed with hot water to remove any traces of acid, and once more sublimed.

Naphthaline, $C_{10}H_8$, forms thin, white, rhombic leaflets of a peculiar odour somewhat like that of storax, and of a burning taste. After fusion and solidification it appears as dazzling white crystalline masses of sp. gr. 1·151. It melts at 79° and boils at 216° to 218°. It is insoluble in cold water, very slightly soluble in hot water, easily soluble in boiling alcohol, benzol, in the volatile and the fatty oils, and in acetic acid.

Anthracene oil when cold forms a greenish-yellow mass, of a buttery consistence, consisting, besides oils of high boiling points, of naphthaline, methylnaphthaline, anthracene, phenanthrene, acenaphthine, diphenyl, methylanthracene, pyrene, chrysene, retene, fluorene, acridine, &c. The anthracene oil is let cool, when crude anthracene crystallises out and is separated from the oils in a filter-press. This 28 per cent. crude anthracene is dissolved by heat (in a double pan, arranged for steam-heating and water-cooling and fitted with an agitator) in 120 per cent. creosote oil, from which the phenols have been removed by treatment with soda-lye. This creosote oil, boiling at 220° to 320° is very suitable for removing paraffine from anthracene. The solution of paraffine is stirred until cold with water refrigeration and is then forced through a filter-press. The product so obtained contains 36 to 40 per cent. of actual anthracene. If it has to be brought to a higher grade this can be effected by a repeated washing in tar oils, but in this manner much anthracene is dissolved. A pure product is obtained by distilling the 36 per cent. anthracene with caustic potassa at 30 per cent. The anthracene is distilled in horizontal cylinders of wrought-iron or cast-iron, 1·2 metre in diameter, 2·2 metres long, and containing about 26 hectolitres. The fire-gases pass through two channels at the bottom of the cylinder, which is protected against the direct action of the flame by fire-proof plates, and pass then along its sides. The distillate runs through an air-cooler into iron pans, in which the anthracene (now 48 per cent.) crystallises. The residue in the cylinder, containing carbazol and potassa, as it is spontaneously inflammable in contact with air, is immediately after distillation drawn off into iron chests, allowed to cool and burnt on an open grate in a furnace for crude potash. Here a flue-dust chamber must be arranged between the chimney and the exit channel in order not to let the fine dust of potash escape into the air. The loss of anthracene in this purification with caustic potassa is, in good kinds, 2 per cent., but in inferior sorts as much as 12 per cent. If a high-grade anthracene is required, this anthracene distilled over potassa can be easily brought up to 70 per cent. by dissolving it in 140 per cent. of heavy benzol, boiling at 140° to 170°, stirring till cold, pressing and recovering the heavy benzol which adheres to it by heating with indirect steam. The total loss in heavy benzol in large works, properly arranged, is 2½ per cent. Instead of heavy benzol, creosote oil washed in soda lye may be used, and after hydraulic pressure the residual creosote oil may be removed by direct steam entering through a perforated false bottom. After the anthracene has been washed the heavy benzol contains large quantities of phenanthrene and heavy oils, as well as of dissolved anthracene, from which the benzol is separated by direct and indirect steam. The crude phenanthrene and the oils running off on hydraulic pressure contain up to 8 per

cent. of anthracene. From phenanthrene it is extracted by adding to the distilled anthracene, during the purification with benzine, about 20 per cent. of phenanthrene. From the press-oils the anthracene may be advantageously recovered by fractional crystallisation during the winter.

Anthracene, $C_{14}H_{10}$, melts at 210° to 213°, and boils at 360°. It is insoluble in water, slightly soluble in alcohol, ether, and benzol, but more freely in toluol.*

Organic Colouring Matters.—Up to the middle of the present century, organic colouring matters were obtained solely from plants and from a few animals (cochineal, &c.) With the discovery of aniline violet in 1856 by Perkins, tar-colours were added to those from natural sources. These artificial products have superseded to some extent several of the natural colours, alizarine, the colouring principle of madder, being now almost exclusively obtained from coal-tar.

Red Colours.—*Madder.*—Madder is the root of the *Rubia tinctorum*, a perennial plant cultivated in Southern, Central, and Western Europe; while in the Levant the *R. peregrina*, and in the East Indies and Japan the *R. mungista* (mungeet), are partly cultivated, partly met with in the wild state. According to researches made in England, the dye imported under the name of mungeet from India is not the root, but the reedy stem of a species of *Rubia*, and as a dye it is inferior. The native country of the madder plant is the Caucasus. All these plants are perennial. The root varies in length from 10 to 25 centimetres; it is not much gnarled, and is generally a little thicker than the quill of a pen. Externally the root is covered with a brown bark; internally it exhibits a yellow red colour. Madder is met with in the trade as the root (technically *racine*, if European), and in powder exhibiting a red-yellow colour, and possessing a peculiar odour. Avignon madder, however, has hardly any smell; but the odour is particularly marked in Zeeland, or so-called Holland, madder. The powdered madder is always kept in strong oaken casks, so as to exclude air and light. The best kind of madder is that grown in the Levant (Smyrna and Cyprus), and met with in the trade under the name of *lizari* or *alizari*, in roots, which are usually rather thicker than the roots of the European varieties, owing partly to the fact that the Levant madder is generally of four to five years' growth, while in Europe the roots are of two to three years' growth only. Dutch madder, chiefly grown in the province of Zeeland, is met with decorticated (*robé*), the outer bark and sometimes the splint bark having been removed. The well-dried roots are broken up by means of wooden stampers moved by machinery, to reduce the bark and splint bark to powder, while the very hard internal portion of the root is left untouched, this being separated from the powder by means of sieves. The powder is put into casks and termed *beroofde*. During the last ten or twelve years the old madder sheds (*meestoven*) in Zeeland have been superseded by large manufactories, in which the madder root is treated as it is in the Vaucluse (France), and ground up entirely, so that the former distinct qualities of madder are no longer met with. When the whole root is pulverised the madder is termed *onberoofde, non robé*. Besides the Dutch madder, that from Alsace and from the Vaucluse, Avignon, occurs very largely in the trade. What is known as *mull* madder is the refuse and dust from the floors of the works, and is the worst quality. In addition to colouring matter, madder contains a large quantity of sugar, of which W. Stein (1869) found as much as 8 per cent. While it was formerly considered that madder contained no less than five different colouring substances, it appears from recent researches that this root in the fresh state only contains two pigments, viz., ruberythrinic acid (formerly termed xanthin) and purpurine. According to Dr. Rochleder, the former of these is converted under the influence of

* For further particulars on the primary coal-tar products the reader may consult G. Lunge, *Coal-Tar and Ammonia*, Gurney & Jackson, London; and *Anthracene, its Properties, &c.*, by G. Auerbach, edited by W. Crookes, F.R.S., &c.: Longmans, London.

a peculiar nitrogenous substance present in the madder root into alizarine—the essential colouring matter of madder—and into sugar:—

$$\underbrace{C_{26}H_{28}O_{14}}_{\text{Ruberythrinic acid.}} + 2H_2O = \underbrace{C_{14}H_8O_4}_{\text{Alizarine.}} + \underbrace{2C_6H_{12}O_6}_{\text{Sugar.}}$$

According to the researches of Graebe and Liebermann, alizarine is a derivative from anthracen, $C_{14}H_{10}$, the formula of the former being $C_{14}H_8O_4$. As elsewhere mentioned, the same chemists have succeeded in converting anthracen into alizarine (169). Alizarine is yellow, but becomes red under the influence of alkalies and alkaline earths. Madder contains a red pigment, purpurine, or rubiacine, $C_{14}H_8O_5$, which by itself, as well as in combination with alizarine, yields a good dye.*

Madder Lake.—We understand by this term a combination of alizarine and purpurine (the colouring matter of madder) with basic aluminium salts. Madder lake is prepared by first washing madder with water, distilled, or at least free from lime salts, next exhausting the dye-stuff with a solution of alum, the liquor thus obtained being precipitated with sodium carbonate or borax. The bulky precipitate, having been collected on a filter, is thoroughly washed and dried.

Flowers of Madder.—The preparation made from madder on the large scale, and known in the trade as flowers of madder (*fleur de garance*), is obtained from the pulverised madder by steeping it in water, inducing fermentation of the sugar contained in it, and next thoroughly washing the residue, first with warm, next with cold water. The residue, after subjection to hydraulic pressure to remove the water, is dried at a gentle heat, and having been pulverised again, is used in the same manner as madder for dyeing purposes. The operation of dyeing with the flowers of madder requires a less elevated temperature of the contents of the dye-beck. It would appear that by the preparation of the flowers of madder the pectine substances of the root are eliminated, which otherwise become insoluble during the operation of dyeing.

Azale.—When flowers of madder are treated with boiling methylic alcohol (wood-spirit), the solution obtained filtered, and water added to the filtrate, a copious yellow precipitate is obtained, which having been washed with water and dried constitutes the material known as azale (from *azala*, Arabian for madder), which has been suggested for use as a dye material in France. Probably this substance is crude alizarine; as obtained from madder or garancine, it is sometimes met with in the trade under the name of Pincoffine, having been first discovered and prepared by Mr. Pincoffs at Manchester.

Garancine.—This preparation of madder contains the colouring principles of the root in a more concentrated, pure, and more readily exhaustible state. In order to prepare garancine, madder (generally this term is given to the pulverised root) is first moistened uniformly with water, and next there is added ½ part of sulphuric acid diluted with 1 part of water. This mixture is heated by means of steam to about 100° for one hour, and the magma then thoroughly washed with water for the purpose of eliminating all the acid. This having been done, the garancine is submitted to hydraulic pressure for the purpose of getting rid of the greater part of the water, after which the material is dried and lastly ground to a very fine powder. By the action of the sulphuric acid some of the substances contained in madder, and more or less interfering with its application as a dye, are eliminated in the washing of the garancine, while the colouring matter remains mixed with the partly carbonised organic substances. As regards its tinctorial value 1 part of garancine may be taken as equal to 3 to 4 parts of madder.

Garanceux.—As madder when employed in dyeing does not become quite exhausted, the fluids of the dye-beck are strained from the solid residue, and this is treated with half

* Mungistine, $C_{16}H_2O_6$, is found in madder from India (munjeet), and dyes like alizarine.

of its weight of sulphuric acid. The mass is next treated as has been described under garancine, and constitutes after drying what is known as *garanceux*, being used generally for the production of what are termed *sad* colours (black, deep brown, lilac). As a matter of course garanceux is of less tinctorial value than garancine.

Colorine.—The substance met with in commerce under the name of colorine is the dry alcoholic extract of garancine, and consists essentially of alizarine, purpurine, fatty matter, and other substances soluble in alcohol present in garancine. E. Kopp commenced some years since to exhaust madder with an aqueous solution of *sulphurous* acid, thereby obtaining the pigments of madder in a (for technical purposes) pure condition. These preparations, which are already extensively used, are distinguished as: Green alizarine (*Alizarine verte*), which from Alsace madder is obtained to an amount of about 3 per cent., containing with the alizarine a green resinous material; yellow alizarine (*Alizarine jaune*), the former substance without the resinous material, this having been eliminated by suitable solvents, as purpurine and flowers of madder. The tinctorial value of purpurine amounts to 10 times and that of the green and yellow alizarine to 32 to 36 times that of madder. Madder of good quality yields on the large scale—*

Purpurine	1·15 per cent.
Green alizarine	2·50 „
Yellow alizarine	0·32 „
Flowers of madder	39·00 „

Safflower.—The drug to which this name is given consists of the dried petals of the flowers of the *Carthamus tinctorius*, a thistle-like plant belonging to the family of the *Synantheræ*, a native of India, and cultivated in Egypt, the southern parts of Europe, and also to some extent in parts of Germany. Safflower contains a red matter, carthamine, insoluble in water, and also a yellow substance soluble in that liquid. The quality of this drug is better according to its greater purity from mechanical admixtures, such as seeds, leaves of the plant, &c. Carthamine, $C_{14}H_{16}O_7$, or *Rouge végétal*, is prepared in the following manner:—The safflower is exhausted with a very weak solution of sodium carbonate, and in this fluid strips of cotton-wool are dipped, after which the strips are immersed in vinegar or very dilute sulphuric acid for the purpose of neutralising the alkali. The red-dyed cotton strips are next washed in a weak solution of sodium carbonate, and the solution thus obtained is precipitated with an acid; the carthamine thrown down is first carefully washed, and next placed on porcelain plates for the purpose of becoming dry. Carthamine when seen in thin films exhibits a gold-green hue, while when seen against the light the colour is red. When carthamine has been repeatedly dissolved and precipitated it is termed safflower-carmine. Mixed with French chalk (a magnesium silicate), carthamine is used as a face powder. Safflower is used for dyeing silk, but the red colour imparted is, although brilliant, very fugitive.

Carthamine is used for red tape, as the exact shade preferred by consumers has not been obtained from coal-tar colours.

Cochineal, or Cochenille.—This substance is the female insect of the *Coccus cacti* found on several species of cacti, more especially on the Nopal plant and the *Cactus opuntia*. This insect and the plants it feeds on are purposely cultivated in Mexico, Central America, Java, Algeria, the Cape, &c. The male insect, of no value as a dye material, is winged, the female wingless. The female insects are collected twice a year after they have been fecundated and have laid eggs for the reproduction of young, and are killed either by the aid of the vapours of boiling water or more usually by the heat of a baker's oven. Two varieties of cochineal are known in commerce, viz., the fine cochineal or *mestica*, chiefly gathered in the district of Mestek, a province of Honduras, on the Nopal plants there cultivated; and the wild cochineal, gathered from cactus

* Since the introduction of artificial alizarine the cultivation of madder has been almost abandoned.

plants which grow in the wild state. This latter variety is of inferior quality. Cochineal appears as small deep brown-red grains, at the lower and rather flattened side of which the structure of the insects is somewhat discernible. Sometimes the dried insect is covered with a white dust, but frequently the material is met with exhibiting a glossy appearance and black colour. The white dust, very frequently fraudulently imparted by placing the grain with French chalk or white-lead in a bag, is, according to the results of microscopical investigation, the excrement of the insect, exhibiting when seen under the microscope the shape of curved cylinders of very uniform diameter and a white colour. Cochineal contains a peculiar kind of acid—carminic acid—which, by the action of very dilute sulphuric acid and other reagents, is split up into carmine-red (carmine)—also present in the insect, together with the acid—and into dextrose—

$$\underbrace{C_{17}H_{18}O_{10}}_{\text{Carminic acid.}} + 3H_2O = \underbrace{C_{11}H_{12}O_7}_{\text{Carmine-red.}} + \underbrace{C_6H_{12}O_6}_{\text{Dextrose.}}$$

What is commonly termed carmine is prepared by exhausting the cochineal with boiling water; to the decanted clear fluid alum is added, after which it is allowed to settle. By another method carmine is prepared by exhausting the pulverised cochinea with a solution of sodium carbonate; white of egg is next added to this solution for the purpose of clarifying it, and afterwards the solution is precipitated with an acid. In either case the washed precipitate is next dried at 30°. So prepared, a finer and better kind of carmine is obtained, but the common carmine—carmine lake and round lake—is prepared by treating an aluminous solution of cochineal with sodium carbonate; the larger the quantity of alumina contained in these preparations, the coarser the quality.

Lac Dye.—This dye-stuff is obtained from a resinous substance, stick or grain lac, or gum resin, and is derived from a variety of the cochineal insect in the following manner:—The *Coccus laccæ*, a native of India, pierces the branches of certain kinds of fig-trees, from which a milky juice exudes, which, while becoming inspissated, encloses the insects, and at last forms a hard resinous mass tinged with the dye-stuff contained in the insects. This pigment is extracted from the resinous matter by means of a solution of sodium carbonate, and the solution obtained is precipitated by alum solution. The lac dye is not very different from cochineal.

Lac shades are somewhat more permanent than those obtained from cochineal, as the carminic acid is accompanied by resinous matter.

Tyrian Purple.—The secretion of the purple snail, which on exposure to sunlight forms the "purple" of antiquity, is not now an article of commerce.

Weed Colours.—By orchil, or archil and cudbear (called persio on the Continent), we designate red dyes which are met with in commerce in pasty masses. Orchil is prepared from several kinds of sea-weed, *Roccella tinctoria*, *R. fuciformis*, *R. Montagnei*, *Usnea barbata*, *Usnea florida*, *Lecanora parella*, *Unceolaria scruposa*, *Ramalina calicaris*, *Gyrophora pustulata*, and others, which having been well dried, are first ground to a very fine powder. This is mixed with ammonia and left to enter into putrefactive fermentation. The ammonium carbonate* acting upon the peculiar acids—lecanoric, alpha- and beta-orcellic, erythrinic, gyrophoric, evernic, usninic, &c.—contained in these sea-weeds, converts these non-nitrogenous substances into orcine, $C_7H_8O_2$, this reaction being accompanied by the elimination of water, and usually also with the elimination of carbonic acid. By taking up nitrogen and oxygen orcine is converted into orceine, $C_7H_7NO_3$, constituting the essential colouring matter of orchil. This substance appears as a red paste, exhaling a peculiar violet odour (*viola odorata*) and having an alkaline taste. Before the coal-tar colours were discovered this dye material was prepared chiefly in England and France from

* Stale urine, or *lant*, was formerly used instead of solution of ammonia.

weeds collected on the Pyrenees, or imported from the Canary Islands, or from Lima and Valparaiso. Cudbear, or red-indigo, is much the same kind of product as orchil, from which it differs mainly in being freed from all excess of ammonia and from moisture, and in being reduced to a fine powder; it was formerly prepared in Scotland from sea-weeds found on the coast. At a later period it was made in large quantity in Germany, in France, and in England. Persio was a red violet powder. Some ten years ago two preparations of orchil were brought into commerce under the names of orchil carmine and orchil purple (*pourpre Français*). These substances contained the orchil dyes in a very pure condition. Since the tar-colours have made their appearance the dyes obtained from the sea-weeds, very beautiful but very perishable colours, have in a great measure become obsolete.

Less Important Red Dyes.—Among the less important red dyes and colouring matters are the alkanet root (*Anchusa tinctoria*); dragon's blood, a red-coloured resin from *Dracaena draco;* harmala red from the seeds of the *Peganum harmala*, a plant growing in the Steppes of Russia; chica red, or carajura, from the leaves of the *Bignonia chica*, a tree growing in Venezuela; purple-carmine, or murexide, obtained from uric acid by treating it with oxidising substances (nitric acid for instance) and next with ammonia.

Murexide produces reds and purples equal to the aniline dyes, but it is more expensive, and the supply of those guanos which are rich in uric acid is falling off.

Red Woods.—There are two distinct classes of red woods used by dyers and printers, by the manufacturers of red inks and of certain pigments. On the one hand are the soft woods, all produced by different species of the genus *Caesalpinia.* The principal kinds are Pernambuco wood, Brazil wood, peach wood, Lima wood, Nicaragua wood, Santa Martha wood, Brazilette and Sapan wood. All these except the last are produced in Central and South America. Sapan is a product of India and Siam. The colouring matter of these woods, Brasiline, ($C_{32}H_{18}O_7$ according to Kopp, but to Liebermann $C_{16}H_{14}O_5$), crystallises in small colourless needles, but the watery solution, on exposure to the air, and especially on boiling or in presence of alkalies, turns crimson.

In dyeing, a very fine but fugitive red colour is obtained from the red woods.

The red woods are extensively used for the production of *red inks.* For this purpose there are taken 250 grammes red wood, 30 grammes alum, 30 grammes tartar, and 2 litres water, and the decoction is boiled down to 2 litres. The liquid is filtered; and for those who like a perfectly limpid ink it is now ready for use. Those who prefer inks which may clog in the pen and dry slowly add 30 grammes gum-arabic and 30 grammes sugar-candy. A finer and more permanent ink is obtained by dissolving 2 decigrammes carmine in 15 grammes liquid ammonia. At present red inks are made simply with solution of magenta to which a little alum has been added, or by dissolving aurine (rosolic acid) in sodium carbonate, or simply with eosine alone. Eosine ink is made by dissolving 1 part eosine in 150 to 200 parts boiling water. Violet aniline ink is obtained by dissolving 1 part soluble aniline violet blue in about 300 parts of water.

Brasilein, $C_{16}H_{12}O_5$, an oxidation product of brasiline, forms small dark crystals with a greyish metallic lustre, which dissolve in hot water with a bright rose colour and an orange fluorescence.

The second class of red woods, the hard woods, comprise barwood, camwood, sanders—or santalwood—and calliatura wood. The colouring matter of these woods is very sparingly soluble in water and is accompanied with a yellow principle, so that they dye tones more inclining to a scarlet. Barwood and camwood are obtained from Africa, and are both said to be the product of *Baphia nitida*, though the colouring matter of camwood is found in practice to be the more soluble. They contain 23 per

cent. of colouring matter. In like manner santalwood and calliatura are alleged to be identical, the tone of the colour being modified, perhaps by difference of soil. Both are obtained from India. Their colouring principle, santaline, contains $C_{17}H_{16}O_6$.

The dyewoods of whatever colour are met with in commerce in four different states; in chips, in raspings, in liquid extracts, or in solid or paste extracts. These different preparations are used according to the texture of the materials to be dyed or printed.

Most woods require after chipping or rasping to lie exposed to the air for some time, and to expedite the process they are sprinkled with water. This addition is carried to such a height that it becomes a fraud.*

The liquid extracts of the woods are often found to contain treacle (beet), dextrine, sodium sulphate, and extracts of materials of little tinctorial value, such as of chestnut, and quebracho. Extract of sumac is rarely added.

The proportion of the ash found in an extract is no better guide to its quality than is the specific gravity.

For detecting and determining treacle, starch, sugar, and dextrine, L. Brueh proceeds as follows: from 1 to 5 grammes of the extract dried at 100° are treated with absolute alcohol until the alcoholic solution no longer gives colour reactions. The sugar and the dextrine remain in the residue along with other colouring matters.

Blue Colouring Matters.—*Indigo.*—Indigo is the chief blue dye. Although known to the Romans and Greeks, who used it for painting purposes, it was not employed as a dyestuff in Europe until about the middle of the sixteenth century. Indigo is a substance which is widely dispersed in the vegetable kingdom. It is found in large quantity in the leaves of several species of the anil plants, *Indigofera*, belonging to the family of the *Papilionaceæ*. Indigo is also obtained from woad, *Isatis tinctoria*, *Nerium tinctorium*, *Marsdenia tinctoria*, *Polygonum tinctorium*, *Asclepias tingens*, &c. The indigo is not met with in the plants ready formed, but is generated when the freshly-pressed juice of the plant is exposed to the action of the atmosphere.

According to the results of a series of experiments, it appears that in the living plant the colourless pigment is present in combination with a base, lime or an alkali. Dr. Schunck states that the indigo plant contains a material which he has termed indican, which either by fermentation or by the action of strong acids is converted into indigo blue and a peculiar kind of sugar, indigo glycine, according to the following formula—

$$\underbrace{C_{52}H_{62}N_2O_{34}}_{\text{Indican.}} + 4H_2O = \underbrace{C_{16}H_{10}N_2O_2}_{\text{Indigo blue.}} + \underbrace{6C_6H_{10}O_6}_{\text{Indigo glycine.}}$$

The indigo of commerce is prepared from the indigo plants in the East and West Indies, Southern and Central America, Egypt, and other parts. In Hindostan indigo is prepared from the *Nerium tinctorium*. The following five varieties of the indigo plant are more particularly employed for the preparation of this dye material: —*Indigofera tinctoria*, *I. anil*, *I. disperma*, *I. pseudotinctoria*, and *I. argentea*. The plant requires a warm climate and a soil so situated that it is not liable to become inundated. When the plants have grown to maturity they are cut down with a sickle close to the soil and transferred to the factory, where the indigo is extracted from the plant by the following process:—The factory is fitted with large water tanks, filtering apparatus, presses, a cauldron, drying-room, and, lastly, with fifteen to twenty tanks of brickwork laid in hydraulic cement and plastered inside with the same material. Into these tanks the branches, twigs, and the leaves are placed, and water is run in, care being taken to force the green plants down under the water by the aid of stout wooden balks wedged tight against the sides of the tanks. At the usual high tempera-

* Compare Slater, *Manual of Colours:* Lockwood & Son, London.

ture of the air in the tropical regions fermentation soon sets in, and the liquid contained in the tanks assumes a bright straw-yellow or golden-yellow colour, a large quantity of gas is evolved, and after a lapse of nine to fourteen hours, the liquid, having become of a deeper yellow hue, or almost the colour of sherry wine, is run from the fermenting tanks into a very large tank of similar construction, into which, when as full as may be judged convenient, a number of workmen enter, provided with long bamboo poles, and commence stirring the fluid vigorously for the purpose of exposing it as much as possible to the action of the air. During this operation, continued for some two or three hours, the colour of the liquid gradually changes to pale green, and the indigo may then be seen suspended in the liquid in very small flocks. The liquid is then left to stand, and the suspended matter gradually subsiding, the water is gradually run off by the aid of taps or plugs fitted into the tank at different heights. At last the somewhat thick, yet fluid, precipitate of indigo is run into a cauldron, where it is boiled for about twenty minutes in order to prevent it fermenting a second time, for by this second fermentation it would be rendered useless. The magma is left in the cauldron over night and the boiling resumed next day, and then continued for three to four hours, after which the indigo is run on to large filters, consisting first of a layer of bamboo, next mats, and on these stout canvas, all placed in a large masonry tank. Upon the canvas is left a thick, very deep blue, nearly black paste, which is thence taken and put into small wooden boxes, perforated with holes and lined with canvas; a piece of canvas is put on the top of the paste, and next a piece of plank is fitted closely into the box. So arranged, a number of these are placed under a screw-press for the purpose of eliminating, by a gradually increased pressure, the greater portion of the water, and thus solidifying the pasty material. On being removed from these boxes the cakes of indigo are transferred to the drying-room, and there, daylight and direct sunlight being carefully excluded, gently dried by the aid, in some cases, of artificial heat. In order to prevent the cracking of the cakes, the drying has to be effected very gently, and lasts usually for some four to six days. The dried cakes of indigo are next packed in stout wooden boxes and then sent into the market. The exhausted plants are used for a manure, for although the boughs on being planted in the soil would again grow, they would not yield either in quality or quantity enough indigo to pay the expenses of culture. 1000 parts of fluid from the fermenting tanks yield 0·5 to 0·75 parts of indigo.

Properties of Indigo.—The indigo met with in commerce exhibits a deep blue colour, dull earthy fracture, and when rubbed with a hard substance (the better kinds of indigo even when rubbed with the nail of the thumb) give a glossy purplish-red streak. In addition to a larger or smaller quantity of mineral substances, indigo contains a glue-like substance, or indigo glue; a brown substance, indigo brown; a red pigment, indigo red; and the indigo blue, or indigotine, $C_{16}H_{10}N_2O_2$, the peculiar dye material for which the drug is valued. The quantity of indigo blue contained in the several kinds of indigo of commerce varies from 20 to 75 and 80 per cent., and averages from 40 to 50 per cent. Indigo may be purified according to Dumas' process by digestion in aniline, whereby the indigo-red and indigo-brown pigments are dissolved and eliminated. According to Dr. V. Warther,* Venetian turpentine, boiling paraffine, spermaceti, stearic acid, and chloroform, are, at high temperatures, solvents for indigo blue.†

Testing Indigo.—The quality of indigo is ascertained by its deep blue colour and lightness.‡ G. Leuchs found that in forty-nine samples of this material the best contained 60·5 per cent., the worst 24 per cent. of indigotine, the specific gravity of the

* See *Chemical News*, vol. xxiii. p. 252.

† See also *Chemical News*, vol. xxv. p. 58, "On the Solubility of Indigo (Indigotine) in Phenic Acid."

‡ See *Chemical News*, vol. xxiv. p. 313.

former being low and of the latter high. Indigo should float on water, and when of good quality it should not, on being broken to pieces, deposit at the bottom of the vessel filled with water in which it is contained a sandy or earthy sediment. On being ignited, indigo should leave only a comparatively small quantity of ash. When suddenly heated, indigo should give off a purplish-coloured vapour, sublimed indigotine, and the drug should be perfectly soluble in fuming sulphuric acid, yielding a deep blue fluid. That kind of indigo which on being rubbed with a hard body exhibits a reddish coppery hue is termed coppery-tinged indigo, *indigo cuivré*. In order to test indigo more accurately, a weighed portion is dried at 100° for the purpose of ascertaining the quantity of hygroscopic water contained, which should not exceed from 3 to 7 per cent. Next the dried indigo is ignited for the purpose of ascertaining the quantity of ash it yields. For good qualities of the drug this amounts to 7 to 9·5 per cent. Numerous methods have been proposed by practical dyers as well as by scientific men for the purpose of ascertaining the value of indigo; that is to say, the quantity of indigotine it contains. Some of these processes are either too tedious, and cause great loss of time, or are not sufficiently exact. A commercial sample of indigo may be treated first with water, next with weak acids, then with alkaline solutions and alcohol, and the ash and hygroscopic water having been estimated, the residue of the different operations will be the indigotine, the process being based upon the insolubility of the latter in the different solvents used for the removal of the impurities met with in the sample under examination. Mittenzwei proposes to reduce the indigo by means of an alkali and solution of ferrous sulphate, to pour over the surface of the liquid a layer of petroleum oil for the purpose of excluding air, to take by the aid of a curved pipette a known bulk of the indigo-containing fluid, and to introduce this fluid at once into a test-jar placed over mercury, and containing a known and accurately measured bulk of pure oxygen. As 1 gramme of white indigotine (soluble) requires for its conversion into blue (insoluble) indigotine 45 c.c. of oxygen, the quantity of gas absorbed gives the quantity of indigotine. This method yields very correct results, but requires an experienced manipulator.

For the spectroscopic examination of indigo, Wolff treats 0·5 grammes of the sample to be examined with 5 c.c. of concentrated sulphuric acid, effects its complete solution by shaking up and digestion, and dilutes to 1 litre. The light is measured in a stratum of 1 centimetre in thickness.

Indigo Blue.—This substance, also known as indigotine, may be obtained from the indigo of commerce, either by carefully conducted sublimation, or, as already stated, by treating indigo with lime, ferrous sulphate, and water. The formula of indigo blue is $C_{16}H_{10}N_2O_2$. When indigo blue, in the presence of alkaline substances, is brought into contact with bodies which readily absorb oxygen — for instance, with ferrous sulphate, sulphites, &c.—there is formed, with simultaneous decomposition of water, white indigo, or reduced indigo, $C_{16}H_{12}N_2O_2$. The use of indigo as a dye material is in great measure based upon this reduction. By the action of oxidising substances, such as permanganic acid, chlorine, chromic acid, a mixture of so-called red prussiate of potash (potassium ferricyanide) with potash, soda, oxide of copper, &c., indigo blue is converted into isatine, $C_{16}H_{10}N_2O_4$. Indigo blue dissolves in concentrated sulphuric acid, but becomes thereby radically changed, and cannot be brought back to its primitive state, forming as it does with the acid a chemical compound—sulphindigotic acid, or, as it is termed by dyers, sulphate of indigo. When this acid solution is treated with potassium carbonate there is formed indigo extract, soluble indigo, a deep blue precipitate soluble in 140 parts of cold water. This indigo extract is used as a water-colour pigment; while, mixed with some starch and a little gum-water, it is formed into balls or other suitable shapes and used as washing-blue, ultramarine being also employed for the same purpose.

The present yield of indigo is 4450 tons yearly :—

Bengal, Oude, Madras	3500
Java	300
Guatemala, &c.	550

Artificial Indigo, though of very high theoretical interest, is not technically important, and modifications in the culture and treatment of the indigo-plant are in progress, which are likely to improve the yield, both in quantity and quality, thus reducing the probability of the success of any artificial substitute. It may be mentioned that natural indigo is a product of fermentation, set up by a specific bacillus. Micro-organisms play important parts also, both for good and evil, in dyeing with indigo.

Logwood, or Campeachy.—This dye material is the wood, freed from bark and splint, of the logwood tree, *Hæmatoxylon campechianum*, a native of Central America, and cultivated in several of the West Indian Islands. The colouring matter contained in this wood is called hæmatoxyline, $C_{16}H_{14}O_6$, a pale yellow, transparent, aciculated crystalline body. By itself it is not a pigment, but is a colourable material, which becomes coloured when brought into contact with strong alkalies, more especially with ammonia and the oxygen of the air. The solution of hæmatoxyline in water is quite colourless, but becomes at once purple-red by the smallest addition of ammonia. The colouring matter thus formed is termed hæmateine. Logwood is used for the purpose of dyeing blue and black. Extract of logwood is very frequently prepared. As with other similar extracts, it should be made in vacuum pans withdrawn from the oxidising action of the air, because the hæmatoxyline contained in logwood becomes thereby altered. The makers of the extracts of dyewoods invariably use vacuum apparatus.

Instead of extract of logwood, there has been used since 1880 a preparation known as "hematine," which is probably impure hæmatoxyline. 15 parts of hematine are reputed equal to 100 parts of the best logwood. It gives faster and brighter shades.

Litmus is used for giving a blue tint to lime and white-wash. It is obtained from the same lichens as archil and cudbear. The difference in the preparation is that the fermentation and oxidation have been carried further, and that the red colouring-matter, *orcine*, has been transformed into the blue compound azolitmine—

$$C_7H_8O_2 + NH_3 + 2O_2 = C_7H_7NO_4 + 2H_2O.$$

The fermented mass is mixed with chalk and gypsum, and brought into commerce moulded into small cubes.

The bezettes or turnesol rags, obtained in the South of France from the juice of *Croton tinctorium*, contain a different colouring-matter. They are turned purple-red or dark-green by ammonia. They are used in Holland for colouring cheese, confectionery, liqueurs, &c.

Yellow Colouring Matters.—*Fustic* (Cuba-wood or old fustic) is the wood of a species of mulberry (*Morus tinctoria* or *Maclura aurantiaca*). It is chiefly imported from Cuba and Hayti. The heart-wood, which alone is used, is of a yellow colour, here and there verging to orange. The colour is due to a colourless crystalline compound, *morine*, $C_{12}H_8O_5$, which is found in the wood in combination with lime and a peculiar tannic acid, named morinetannic acid (or Maclurine), $C_{13}H_{10}O_6$, which is found deposited in the wood, sometimes in considerable quantities. Morine takes a yellow colour on exposure to air, or on contact with alkalies. Maclurine, if treated with caustic potassa, is split up into phloroglucine and protocatechutic acid.

Fustic is used for dyeing yellows and blacks, where it serves to correct the blue tone of logwood. It is extensively used as a liquid extract and also as a paste.

Young Fustic (Zante Fustic, Fustet, or Fiset) is a greenish-yellow wood, striped

with brown, obtained from *Rhus cotinus*, a shrub growing wild in the South of Europe, and sometimes named Venetian sumac. Its colouring-matter, fustine, or fisetine,

$$C_{23}H_{10}O_3(OH)_6,$$

is a bright, but rather fugitive dye. It is chiefly used by some woollen-dyers.

Annatto (Annotto, Arnatto, or Orleans) is a yellowish-red colouring matter, formerly much used in silk-dyeing, but now employed only in the manufacture of varnishes and in colouring butter.*

It is sold as a stiff paste, and is obtained from the fruit of *Bixa Orellana*, a shrub native in South America, and cultivated at Cayenne, in the Antilles, and in India. It contains two colouring matters—bixine, a yellow; and orelline, a red ($C_5H_6O_4$).

Berries (*Persian berries*, *French*, *Avignon*, or *Turkey berries*) are the fruit of *Rhamnus infectorius*, *R. saxatilis*, and *R. amygdalinus*, species of buckthorn. They are met with large and full, of an olive-yellow colour, and also smaller, wrinkled and dark-brown. The former kind are collected before full ripeness, whilst the latter are left to dry on the trees. They contain a fine golden-yellow colour, chrysorhamnine, which Bolley regards as identical with quercetine, and an olive-yellow colouring matter, xantho-rhamnine. They are extensively used in calico-printing, chiefly in the form of extract, in staining paper, and in the manufacture of yellow lake.

Turmeric is the dried root of *Curcuma longa* and *C. rotunda*, plants cultivated chiefly in Bengal. The roots, which vary in thickness from that of a quill to a diameter of ½ inch, are wrinkled, and have ring-like swellings at short intervals. They contain 11 to 12 per cent. of curcumine ($C_8H_{10}O_2$), a yellow tinctorial principle.

Weld or Wold; a plant sometimes erroneously confounded with woad, was formerly much used for dyeing moderately fast yellows on silk and cotton with sodium aluminate. Its colouring principle is luteoline.

Quercitron (commonly named "bark" by the dyers) is the rind of *Quercus infectoria*, a species of oak growing in North America. There are two varieties, obtained respectively from Philadelphia and Baltimore, the former being superior. It contains a yellow colouring matter, quercitrine $C_{33}H_{30}O_{17}$, and tannic acid. On treatment with dilute acids, quercitrine splits up into isodulcite (a sugar of the formula $C_6H_{10}O_5$) and quercetine, $C_{27}H_{18}O_{12}$, a bright yellow powder sold as flavine. Quercitron, both in substance, as extract, and as flavine, is more extensively used than any other yellow dye.

Among other yellow dye-wares we may mention *Serratula tinctoria*, dyers' broom (*Genista tinctoria*); wongshy, the seed pods of *Gardenia florida*; puree or Indian yellow, a colour consisting of magnesium euxanthate and free euxanthon, and obtained from the urine of cows fed upon the leaves of the mango. The vegetable yellow colours have been almost entirely superseded by chrysoidine, tropaeoline, picric acid, Victoria yellow, and other coal-tar colours.

Brown, Green, and Black Colours.—Brown colours were formerly obtained from mixtures of reds, yellows, and blues, or of yellows and reds with blacks. Browns are often dyed with catechu and other tanniferous extracts, in conjunction with oxidising agents, such as potassium dichromate, ammonium vanadate, &c. They are also obtained with the so-called "patent colours" (Cachou de Laval) invented by Croissant and Bretonniere.

Black is obtained with ferrous-ferric oxide in conjunction with solutions of tannin or gallic acid, with decoction of logwood and potassium chromate, or, in printing, with aniline black.

Greens were obtained with mixtures of yellows and blues, or with Chinese green (Laokao) from *Rhamnus chlorophorus* and *R. utilis*, and with sap or bladder green from

* For this latter purpose it is utterly improper, as it is made up with stale urine and swarms with bacteria, some of which may be morbific.

the berries of the buckthorn (*Rhamnus catharticus*). The use of green vegetable colours has been much interfered with by the introduction of methyl-green, malachite green, &c.

Ordinary writing ink consists essentially of ferric and ferrous tannates and gallates, held in suspension by means of gum-arabic.*

A good black ink may be obtained by extracting 1 kilo. pulverised gall-nuts and 150 grammes logwood, with 5 litres hot water, dissolving at the same time 600 grammes gum in $2\frac{1}{2}$ litres water and $\frac{1}{2}$ kilo. copperas in 4 kilos. of water. The tannic extract and the solutions of gum and copperas are then poured together, and a few drops of oil of cloves or gualtheria are added and water enough to make up 16 litres.

Tannin Ink is obtained by dissolving 12 grammes tannin, 40 grammes copperas, and 50 grammes gum in 1 litre of boiling distilled water. Iron inks, beside attacking the steel pens, have the defect that the writing in time turns yellow. Hence the proposal to use ammonium vanadate instead of iron salts deserves notice.

Ink from 1000 parts decoction of logwood (1 part wood to water) and 1 part yellow (neutral) potassium chromate, with the addition of a trace of mercuric chloride, is at once cheap, permanent, and beautiful; the colour is a compound of haemateine and chromium oxide.

To obtain the so-called *alizarine* ink, 42 parts galls and 3 parts madder are extracted with water, so as to make up 120 parts of liquid, to which are added 1·2 part indigo sulphate, 5·2 parts copperas, and 2 parts iron pyrolignite solution.

The reddish-blue ink from Rouen (*encre rouennaise*), extensively used in France, consists of a decoction of 750 grammes logwood, 35 grammes alum, and 31 grammes gum in 5 to 6 litres water. Coupier's induline ink is simply a solution of induline in 50 parts of water.

Copying inks are merely strong common inks with a large addition of gum and sugar or glycerine. Inks are prevented from turning mouldy by the addition of a little quinine sulphate, salicylic acid, or phenol.

TAR COLOURS.

Repeated attempts have been made to arrange the colouring matters obtained from coal-tar in natural groups.

R. Nietzki distinguishes:

1. Nitro compounds.
2. Azo colouring matters.
3. Triphenyl methan colouring matters.
4. Indamines and indophenoles.
5. Saffranines and their allies.
6. Aniline black.
7. Indulines and nigrosines.
8. Quinoline and acridine colouring matters.
9. Anthraquinone colouring matters.

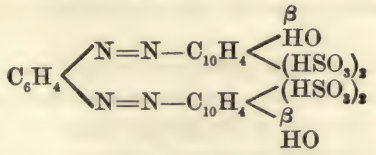
The nitro-compounds contain the group NO_2, *e.g.*, picric acid, binitrocresol.

The azo-colours contain the groups $-N=N-$. The entrance of the azo-group into a hydrocarbon or into a compound similar in its behaviour (*e.g.*, anisol, phenetol) produces in the first place certain coloured compounds which are not true colouring matters, as they do not unite with the animal fibre. This affinity to the fibre is obtained only by the introduction of certain groups, which give the azo-compounds acid or basic properties. On the other hand, the intensity of the colouring matter is generally heightened and the tone is essentially modified.

* Hence has been derived the custom of adding gums or sugars to all inks, even such as are true solutions and do not require to be suspended.

In colouring matters which, besides the benzene group, possess no higher hydrocarbon residue, the colours represented are merely yellow, orange, and brown. Only by introducing the naphthaline residue there are obtained reds, and by its repeated introduction violets and blues. The introduction of groups which are in themselves indifferent (*e.g.*, the methoxyl groups OCH_3) may produce a striking modification of the colouration.

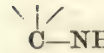
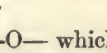
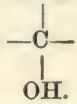
The relative position of the groups is also important. Thus the compound—



has, *e.g.*, a red colour if the benzene nucleus, the meta position, is occupied, but a blue if the para position is taken.

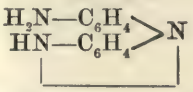
The azo-dyes in technical uses are mostly sulph-acids and behave as acid colours. There are employed in their production the sulph-acid of the diazo-compounds or of the phenoles. In some cases the previously formed azo-compound is converted into a sulph-acid by treatment with sulphuric acid.

The triphenylmethan colouring matters contain, according to Nietzki, the group

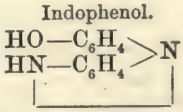
 or  which is to be regarded as the chromogen of the compound. If the salts of the nitrogenous triphenylmethan colours are decomposed by alkalies there occurs an addition of water, and there are formed amido-derivatives of triphenylcarbinol which contain the group  The ring-shaped combination has therefore become open. These carbinol derivatives are generally regarded as the bases of the colouring-matters and the latter as salts of the former. But in truth both possess a distinct constitution, and in consequence quite distinct properties. The carbinol compounds are perfectly colourless, whilst their salts, or more correctly those of their anhydrides, are powerful dyes. The conversion of the carbinol compounds into colouring matters is not effected as easily as the formation of salts from bases and acids, but requires in many cases a prolonged action, which often seems to follow after the mere formation of a salt. Tetramethyldiamidotriphenylcarbinol (the colourless base of malachite green) dissolves first in dilute acids to a colourless liquid. On heating, or on prolonged standing, it becomes intensely green, all the triphenylmethan colouring matters belonging here are para-derivatives—*i.e.*, they contain the nitrogenous or oxygenous groups in the para-position to the methan carbon. Here belong the true aniline colours, such as malachite green.

Indamines and Indophenoles are formed when paradiamines or para-amidophenoles are oxidised in presence of monamines or phenoles. Indamines are formed by oxidation in a neutral, and indophenoles in an acid liquid. Indophenoles form colouring matters in the free state, and their salts are colourless; in indamines the reverse holds good. Both are readily decomposed by an excess of acid with the formation of quinones. Their constitutional formulæ are probably

Indamine.



Indophenol.



Saffranines contain four atoms of nitrogen in their molecule, two of which are in the form of amido groups. Four atoms of hydrogen may be replaced by alcohol radicles,

and two by acid radicles—*e.g.*, of acetyl. They may also be converted into diazo-compounds, in which generally one, but sometimes two, amido groups may be converted into diazo groups.

In all these substitutions the strongly basic nitrogenous group which serves for the formation of the monobasic salts is not attacked. The acetyl derivations of saffranine still form salts, and the primary diazo-compounds have a strongly bibasic character, and contain, therefore, an acid molecule which is not linked to the diazo-group.

The formation of saffranine from paradiamidodiphenylamine, with a simultaneous oxidation with monamines, lets us conclude that in it two benzene nuclei are connected by an atom of nitrogen, that both the amido groups belong to this benzene nucleus, and are in the para-position as regards the atom of nitrogen which connects them.

The saffranines are therefore closely related to the indamines, and are formed from the latter when heated with monamines in an aqueous solution, whilst hydrogen is being split off, and, if no oxidising agent is present, effects a partial reduction of the indamine. The amidised indamines (*e.g.*, toluylene blue) are converted directly on heating with partial reduction into colouring matters resembling saffranine. Their ordinary production depends on the oxidation of one mol. of a paradiamine with two mols. of a monamine.

The mono-acid salts of the saffranines are generally red, but the introduction of alcohol radicles into the amidic groups modifies the colours towards a violet. The introduction of methoxyl and ethoxyl groups into the benzene nuclei changes the tone of the colours in the direction of yellow. Upon animal fibres and upon cotton mordanted with tannin the saffranines take very readily, producing the colour of their mono-acid salts.

The formula for aniline black is not yet decided.

Among the *indulines* and *nigrosines* are included a series of colouring matters formed by the action of certain nitro- and azo-compounds upon aromatic amines and having all blue-grey or black-blue colours. On heating amido-azo-benzol with aniline hydrochlorate to 160°, ammonia is eliminated, and there is formed a violet colour, $C_{18}H_{15}N_3$ (azo-diphenyl blue), which may be regarded as the first link of the induline series.

Flavaniline is ranked among the *quinidine* colours. For *anthracene* colours, see below.

Schultz and Julius arrange the 274 most important colouring matters as follows:—

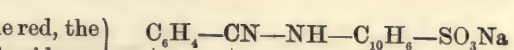
1. Nitroso colours—*e.g.*, naphthol green B (a ferrous sodium salt of nitroso-β-naphthol monosulphuric acid) = $C_{10}H_5\left\{\begin{matrix}SO_3NaNaO_3S\\O\qquad\qquad O\\|\qquad\qquad|\\NO—Fe—ON\end{matrix}\right\}C_{10}H_5$

2. Nitro colours—*e.g.*, picric acid . = $C_6H_2\left\{\begin{matrix}[1]OH\\[2]NO_2\\[4]NO_2\\[6]NO_2\end{matrix}\right.$; Flavaurin = $C_6H_2\left\{\begin{matrix}[1]ONH_4\\[2]NO_2\\[6]NO_2\\[4]SO_3NH_4\end{matrix}\right.$

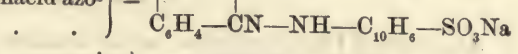
3. Azoxy colours—*e.g.*, sun yellow (*Jaune soleil*), maize, acid curcumine (a sodium salt of azoxystilbene-disulphonic acid) = $\begin{matrix}CH[1]C_6H_3\left\{\begin{matrix}[2]SO_3Na\\[4]N\end{matrix}\right.\\\|\qquad\qquad\diagdown O\\CH[1]C_6H_3\left\{\begin{matrix}[4]N\diagup\\[2]SO_3Na\end{matrix}\right.\end{matrix}$

4. Azo colours—*e.g.*,
 - Aniline yellow, amidoazobenzol hydrochlorate = $C_6H_4\left\{\begin{matrix}[1]NH_2.HCl\\[4]N=N—C_6H_5\end{matrix}\right.$
 - Fast yellow R, acid yellow R, the sodium salt of amido azotoluol-disulphacid = $C_6H_3\left\{\begin{matrix}[2]CH_3\\SO_3Na\\[1]N=N[1]C_6H_2\end{matrix}\right.\left\{\begin{matrix}[2]CH_3\\[4]NH_2\\SO_3Na\end{matrix}\right.$

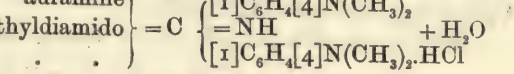
5. Hydrazon colours—*e.g.*, phenanthrene red, the sodium salt of *a*-naphthyl-*a*-sulphacid azo-phenanthreno quinone



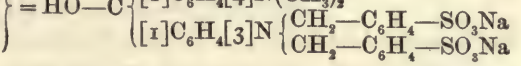
6. Diphenyl methan colours; only auramine (hydrochlorate of imidote tramethyldiamido diphenyl-methan)



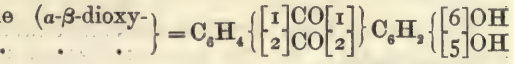
7. Triphenyl methan colouring matters—*e.g.*, fast green (the sodium salt of tetramethyl-diphenyl-pseudo-rosanilinesulpho acid)



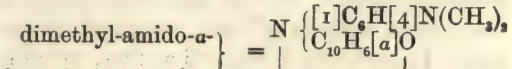
8. Anthracene colours—*e.g.*, alizarine (*a*-*β*-dioxy-anthraquinone)



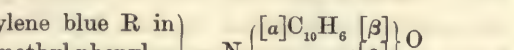
9. Indophenoles — *e.g.*, indophenol, dimethyl-amido-*a*-naphtho-quinone anilide



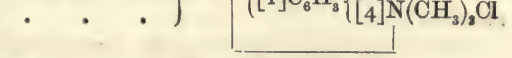
10. Oxazines—*e.g.*, new blue (naphthylene blue R in crystals); fast cotton blue = dimethyl-phenyl-*a*-ammonium-*β*-oxynaphthoxazine



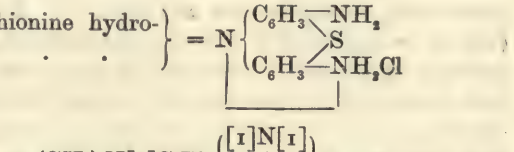
11. Thionine colours, Lauth's violet, thionine hydrochlorate



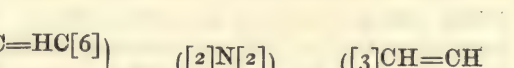
12. Eurhodines—*e.g.*, neutral violet, dimethyl-diamephenazine hydrochlorate . .



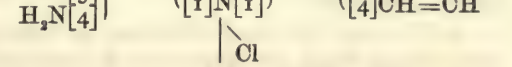
13. Saffranines—*e.g.*, Magdala red, naphthaline red, naphthaline rose, naphthaline scarlet, Soudan red, rosa-naphthylamine (diamidonaphthylnaphthazonium chloride)



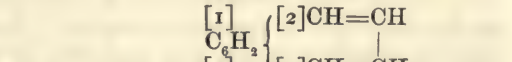
14. Indulines and nigrosines—*e.g.*, fast blue =



15. Artificial indigo =



16. Quinoline and acridine colours—*e.g.*, flavaniline (hydrochlorate of para-amido phenyl and lepidine . .



In research, or for instruction in organic chemistry, such an arrangement is doubtless preferable, but in technology it seems more important to follow the process of manufacture.

1. BENZOL COLOURS.

Commercial benzol contains, besides benzene (true benzol), toluol ($C_6H_5.CH_3$), xylol $C_6H_4(CH_3)_2$, and cumol $C_6H_3(CH_3)_3$.

Nitrobenzol.—On the nitration of benzol there is formed nitrobenzol:

$$C_6H_6 + HNO_3 = C_6H_5.NO_2 + H_2O.$$

On nitrating toluol,

$$C_6H_5.CH_3 + HNO_3 = C_6H_4.NO.CH_3 = H_2O,$$

there are produced three isomeric nitrotoluols, chiefly orthonitrotoluol (boiling point 223°), with small quantities of metanitrotoluol.

The technical nitrobenzol is therefore a mixture of nitrobenzol and nitrotoluol along with nitroxylol. For its production there is run into the benzol, in a cast-iron vessel fitted with an agitator, a mixture of two parts strong nitric acid and sulphuric acid. It must be refrigerated at first, which is effected by letting water flow over the vessel; after a few hours the temperature is gradually let rise to 60–80°. When the reaction is completed the two liquids are allowed to separate, and the nitrobenzol is purified by washing it with water. 100 kilos. benzol yield 135 to 140 kilos. nitrobenzol.

There are three nitrobenzols, corresponding to the different benzols:—1. Light nitrobenzol, boiling between 205 and 210°. It forms the artificial oil of bitter almonds (not to be confounded with the benzaldehyd, $C_6H_5.COH$, prepared from toluol), or mirbane oil (essence de mirbane), sp. gr. = 1·20. It is used in quantity in perfumery and in soap-making, and also in the sophistication of wines. 2. Heavy nitro-benzol, distilling between 210 and 220°, sp. gr. = 1·19. Its peculiar odour prevents its use in perfumery. From this kind the "aniline for reds" is obtained. 3. Very heavy nitrobenzol, distilling between 222 and 235°, sp. gr. = 1·167. Its odour is unpleasant.

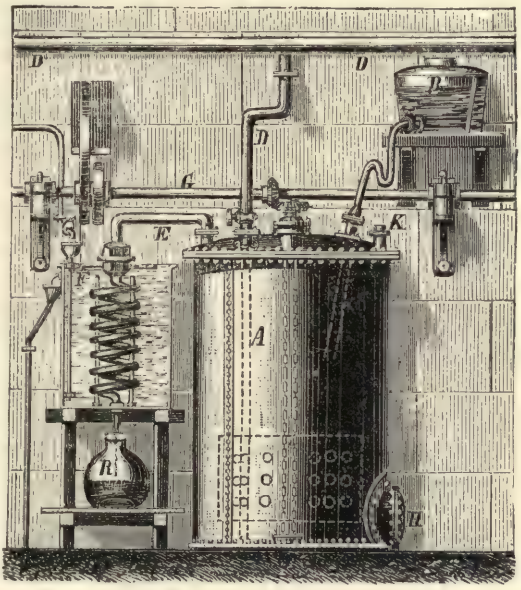
Aniline.—By amidising nitrobenzol there is obtained crude aniline, aniline oil, the initial point for obtaining the aniline colours. It is substantially a mixture of aniline (amidobenzol) ($C_6H_5NH_2$) and toluidene amidotoluol ($C_6H_4 NH_2.CH_3$). It is known in the trade as aniline oil. Pure aniline and pure toluidene alone, form colours only under certain conditions.

Aniline was discovered at Dahme, in Saxony, by Dr. Unverdorben, in 1826, among the products of the dry distillation of indigo, and in 1833 Runge, at Oranienburg, near Berlin, discovered its presence in coal-tar. Runge also discovered that aniline yielded, when brought into contact with a solution of hypochlorite of lime (bleaching powder), a beautiful violet colour; hence the name kyanol (*blue colouring oil*). Fritzsche of St. Petersburg, 1841, thoroughly investigated the substance obtained by Dr. Unverdorben from indigo, ascertained its composition, and called it aniline, from *anil*, the Portuguese name for indigo. In the year 1842 Zinin found that when nitrobenzol was treated with sulphuretted hydrogen there was formed a base which he termed benzidam. The further researches of O. L. Erdmann and Dr. A. W. Hoffmann brought the fact to light that Dr. Unverdorben's crystalline, kyanol, benzidam, and aniline were the same substance, to which the aniline was then finally given. We owe to the extensive researches of Dr. A. W. Hoffmann our present knowledge of aniline and its compounds.

Coal-tar contains 0·3 to 0·5 per cent. of aniline, but its extraction from tar is attended with so many difficulties that it is preferred to prepare aniline from nitrobenzol by a reaction discovered by Zinin—that is to say, to bring nitrobenzol into contact with reducing agents: 1 molecule of nitrobenzol, $C_6H_5N_2O = 123$, yields 1 molecule of aniline, $C_6H_7N = 93$. In practice it is assumed that 100 parts of nitrobenzol yield 100 parts of aniline.

Although sulphuretted hydrogen completely reduces nitrobenzol to aniline, the trade working on a large scale prefers to follow Béchamp's method, the treatment of nitrobenzol with iron-filings and acetic acid. The apparatus in use for carrying out this operation was devised by Nicholson, and is exhibited in Fig. 393. It consists essentially of a cast-iron cylinder, *A*, of 10 hectolitres (220 gallons) cubic capacity. A stout iron tube is fitted to this vessel, reaching nearly to the bottom of the cylinder. The upper part of this tube is connected with the machinery, *G*, while the surface of the tube is fitted with steel projections. The tube serves to admit steam, besides acting as a stirring apparatus. Sometimes, instead of this tube, a solid iron axle is employed, and in this case there is a separate steam-pipe, *D*. Through the opening at *K* the materials for making aniline are put into the apparatus, while the volatile products are carried off through *E*. *H* serves for emptying and cleaning the apparatus. The S-shaped tube connected with the vessel, *B*, acts as a safety-valve. When it is intended to work with this apparatus there is first poured into it through *K* 10 kilos. of acetic acid at 8° B. (=sp. gr. 1·060), previously diluted with six times the weight of water; next there are added 30 kilos. of iron-filings or cast-iron borings, and 125 kilos. of nitrobenzol, and immediately after the stirring apparatus is set in motion. The reaction ensues directly, and is attended by a considerable evolution of heat and of vapours. Gradually more iron is added until the quantity amounts to 180 kilos. The escaping vapours are condensed in *F*, and the liquid collected in *R* is from time to time poured back into the cylinder, *A*. The reduction is finished after a few hours. The resulting thick magma exhibits a reddish-brown colour, and consists essentially of hydrated oxide of iron, aniline, acetate of aniline, acetate of iron, and excess of iron. Leaving the acetic acid out of the question, the process may be elucidated by the following formula:—

Fig. 393.



$$\underbrace{C_6H_5NO_2}_{\text{Nitro-benzol.}} + H_2O + Fe_2 = \underbrace{C_6H_7N}_{\text{Aniline.}} + \underbrace{Fe_2O_3}_{\text{Ferric oxide.}}$$

This magma is either first mixed with lime or is put into cast-iron cylinders shaped like gas-retorts, and submitted to distillation, the source of heat being either an open fire or steam. The product of this operation, consisting of aceton, acetaniline, aniline, nitrobenzol, &c., is rectified by a second distillation, care being taken to collect separately the product which comes over between 115° and 190°; but a product which comes over at between 210° and 220° is very suitable for the preparation of aniline blue. The aniline oil thus obtained is a somewhat brown-coloured liquid, heavier than water, and pure enough for the preparation of the aniline colours. According to Brinmeyer, acetic acid is not necessary, and a very good result may be obtained by mixing nitrobenzol with 60 parts of pulverised iron with acidified water (2 to 2·5 per cent. of hydrochloric acid

upon the weight of nitrobenzol), and leaving this mixture to stand in a retort for some three days before distilling off the aniline oil. In the aniline oilworks of Coblentz Frères, at Paris, nitrobenzol is reduced by the aid of iron-filings, a portion of which have been coated with copper by being immersed in a solution of the sulphate.

The composition of the aniline oil—essentially a mixture of aniline, toluidine, and pseudo-toluidine—depends upon the nature of the benzol and nitrobenzol used for its preparation. The aniline oil boiling between 180° and 195° (sp. gr. = 1·014 to 1·021 = 2° to 3°B.) is prepared from nitrobenzols which boil between 210° and 220°, and the aniline it yields is chiefly used for aniline red; while for aniline blue a very heavy nitrobenzol is employed, and for aniline violet a nitrobenzol which boils at 210° to 225°. The following table exhibits the boiling-points of the substances which have been mentioned :—

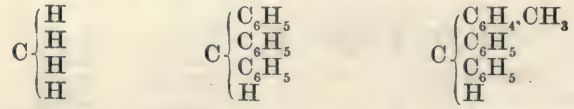
Benzol	80°	Nitro-toluol . . .	225°
Toluol	108°	Aniline	182°
Nitro-benzol . . .	213°	Toluidine . . .	198°

As regards the annual production of aniline oil, it is now (1871) 3,500,000 lbs., of which 2,000,000 lbs. are consumed in Germany, and the remainder in Switzerland, England, and France.

The so-called *pure aniline*, which has been produced on the large scale since 1870, has at 15° the sp. gr. 1·0245. It contains very small quantities of toluidine (not above 1 per cent.), and forms a clear solution in dilute acids. Its chief use is in the manufacture of aniline blue, of methyl aniline and diphenyl amine. It is also used in printing for the production of aniline black.

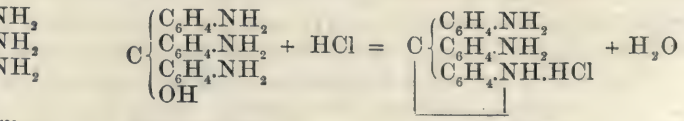
Toluidine corresponds in purity to the aniline described above. It contains a predominating quantity of ortho- or of para-toluidine according to the manner of its preparation. The largest quantity of aniline oil is that "for red," a mixture of aniline with the two toluidines and a little xylidine, which distils over within a range of 10–12°, and has the sp. gr. 1·004–1·006. It consists approximately of 20 per cent. aniline, 40 per cent. toluidine, and 40 ortho-toluidine. Besides aniline for reds there is produced a much smaller quantity of aniline for saffranine, which contains a large relative proportion of aniline, namely, 35 per cent. Its sp. gr. is 1·010, and it distils over at 185–190°. It has a similar composition to the so-called échappés from the manufacture of magenta, which, indeed, are often used for obtaining saffranine.

The most important of the aniline colours are the following :—Aniline red (magenta), called on the Continent and in America by the misleading name of fuchsine, and formerly by the still worse names of azaline and harmaline, belongs to the derivatives of triphenyl methan, $C_{19}H_{16}$, or of tolyldiphenyl methan, $C_{20}H_{18}$.



Methan. Triphenyl methan. Tolyldiphenyl methan.

If in triphenyl methan hydrogen is replaced by NH_2, and again by CH_3,C_6H_5, &c., there are formed leuko-bases, which form with acids colourless salts, but on oxidation pass into colour-bases, yielding coloured salts—*e.g.* :



Paraleukaniline. Pararosaniline. Its hydrochlorate.

Magenta is a mixture of pararosaniline and rosaniline hydrochlorate or acetate, rarely

nitrate or sulphate, the rosaniline being derived from tolyldiphenyl methan—*e.g.*, as hydrochlorate, $C_{19}H_{26}N_3ClO_4$ and $C_{20}H_{28}N_3ClO_4$.

$$C\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH.HCl\end{cases} \quad \text{and} \quad C\begin{cases}C_6H_3.CH_3.NH_2\\C_6H_4.NH_2\\C_6H_4.NH.HCl\end{cases}$$

Salt of rosaniline, with 3 mols. of acid, have an insignificant yellow colour, and are decomposed by water into monacid salts, 2 mols. acid being liberated. By the action of nitrous acid upon the salts of rosaniline there are formed diazo-rosaniline salts, which on boiling in water yield rosolic acids.

Aniline red is produced from aniline oil by treatment with various oxidising agents —*e.g.*, with stannic chloride (Verguin), carbon perchloride (Hofmann and Nathanson), mercuric nitrate (Gerber-Keller), mercuric chloride (Schnitzer), nitric acid (Lauth and Depouilly), antimonic acid (Medlock, Girard, and De Laire), nitrobenzol and nitrotoluol (Coupier). From 100 parts of aniline there are obtained 25 to 30 parts of crystalline magenta.

Arsenic Acid Process.—If a mixture of the diacid arseniates of aniline—

$$AsO\begin{cases}OH\\OH\\ONH_3.C_6H_5\end{cases}$$

of *o*- and *p*-toluidine

$$AsO\begin{cases}OH\\OH\\O.NH_3.C_7H_7\end{cases}$$

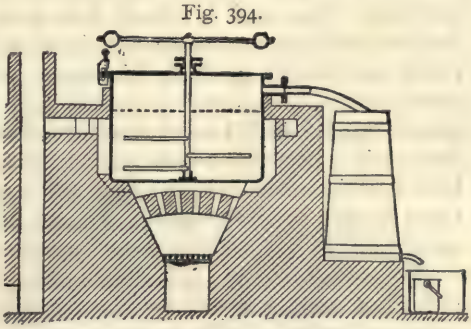
is heated to 180–190°, the acid is reduced, and there is formed a mass of a cantharides green colour, containing the magenta bases: pararosaniline, methyl-pararosaniline, and probably dimethyl-pararosaniline; the phosphine bases: chrysaniline and methyl-chrysaniline; and the induline bases: melaniline and mauvaniline, in the state of arsenites and arseniates. The formation of pararosaniline is effected by oxidising out the hydrogen atoms from a mixture of 1 mol. paratoluidine and 2 mols. aniline according to the following equation:—

$$\begin{cases}C_6H_4.NH_2\\H\\H\\H\end{cases} + 2H.C_6H_4.NH_2 + O_3 = 2H_2O + C\begin{cases}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\\OH\end{cases}$$

The formation of methyl-pararosaniline (rosaniline), and of dimethyl-pararosaniline (rosotoluidine), ensues from corresponding mixtures of bases.

The melting-pot used in the arsenic process (Fig. 394), 1 metre high, consists, according to Schoop, of cast-iron; the cover can be raised by means of a pulley. The exit-pipe for the distillate is screwed to one side. The contents of the melting-pot are kept in motion during the process by means of an agitator. A smaller opening serves for taking out specimens of the melt. The pan is built up in such a manner that the flame gases stream through a perforated arch against the bottom of the pan, and thence pass up uniformly along its sides, and are finally led through a ring-shaped channel to the chimney.

Fig. 394.



The following is the composition of two approved aniline oils for reds:—

	A.		B.
Aniline	22·0	...	16·3
Orthotoluidine . . .	58·4	...	68·4
Paratoluidine . . .	19·6	...	23·3
Sp. gr.	1·0020		1·0000

The pan is charged with 700 kilos. arsenic acid at 195° Tw.; 300 kilos. recovered arsenic acid of the same strength, 300 kilos. aniline for reds, and 200 kilos. of distillate from former charges. If the pan is cold the mixture coagulates to a thick jelly. Generally, the pan is so warm from former operations that the mixture remains liquid. The fire is kindled at 6 A.M., so that the distillation begins at 1 or 2 P.M. After twenty hours (when 20 to 25 jugs of distillate have been collected) the fire is raised until 20 litres distil over hourly. After 400 litres in all have passed over, the melt will have become thick. Samples are now taken frequently, and the melt is broken up as soon as it becomes pasty. The cover is quickly drawn up and the contents are baled out upon sheet-iron trays by means of copper scoops. The melting takes thirty-six hours. As soon as the melt becomes pasty the fire is only kept up faintly, as the heat of the pan is sufficient to complete the reaction. Only prolonged experience enables the operator to judge when the melting should be stopped. If the melt is too thin the yield will be low; if it has become too thick it is a hard task to dig it out of the pan with chisels. During baling out, the copper scoops are frequently plunged into cold water to prevent the melt from adhering. The workman protects himself during baling out against the dense aniline vapours by a sponge moistened with acetic acid and fixed over the mouth and nostrils. The operator is also changed every two or three minutes. The melt when cold is broken up into pieces the size of a fist. The average weight is 88·6 kilos. The fracture of the melt is conchoidal, it is brittle, and has a golden lustre. The distillate is collected in a large parting funnel, and there are added to it 100 kilos. of salt. The oil then rises readily to the surface; the solution is drawn off and diazotised after the proportion of aniline present has been ascertained, precipitated with a solution of naphthol and worked up for naphthol orange. The stratum of oil is rectified in a still and used for future melts. The distillates from the red oils A and B contain respectively:

	A.	B.
Aniline . . .	29 per cent.	21 per cent.
Orthotoluidine . .	71 „	79 „
Paratoluidine . .	— „	— „
Sp. gr. at 18°	1·0076	1·0057

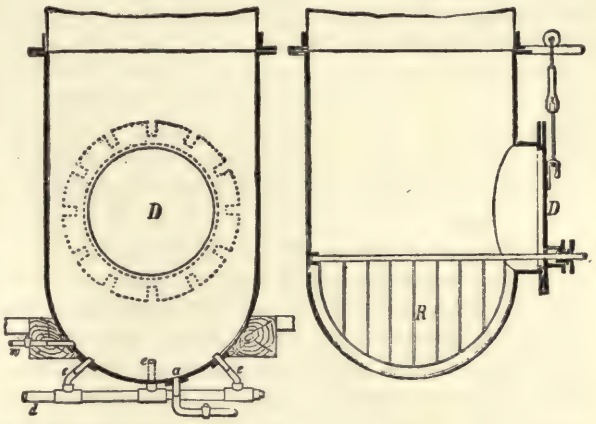
The distillates may be worked up more advantageously for safranine (see below). On an average a melt yields 220 kilos. of distillate.

The melt is now ground up wet to a fine mud, for which two hours are generally required. The mud is let off into a monte-jus and passed through a filter-press. Whilst the filtrate is concentrated in an iron pan, to recover the arsenic acid, the press-cakes are stirred up with lukewarm water and filtered again. The filtrate now obtained is used in grinding up the next melt. As a matter of course the melt is ground up in small lots of about 100 kilos. each. The crude melt after being thus treated is a greenish-yellow powder, which is twice subjected to a lixiviation with boiling water in the extraction pan (Figs. 395 and 396). Whilst the melt was formerly baled in open vessels by means of steam, and afterwards in closed horizontal cylinders, which allowed of extraction at a slight pressure, upright lixiviators are now preferred.

This vessel consists of a cast-iron foot-piece with an opening for introducing the pulverised melt, and can be closed with the lid D running upon rails. On the semi-globular bottom of this foot-piece there are three inlets for steam, *e*, of 37 mm. diameter, arranged symmetrically and fed from the common steam pipe, *d*. A little higher is the inlet for water, *w*, and at the lowest point the outflow, *a*. The cover, D, which closes the circular feeding-hole is secured with screws, and is provided with a stuffing box, which serves for the axle of the agitator, R, which is occasionally moved by hand. Above the foot-piece rises the upper cylindrical part of the apparatus,

riveted together with boiler plates, which is closed above with a slightly arched cover. At about three-quarter height of the entire apparatus is a small escape-cock which shows the height to which the pan is filled with water. In addition there is a manometer attached to the cover, to indicate the pressure within. The upper portion of boiler plate is screwed down to the foot-piece. The entire apparatus, which is 1 metre in diameter and $4\frac{1}{2}$ metres in height, rests by means of its lower hemispherical part upon a solid frame of wood. At three-quarters height the apparatus passes through a second frame to prevent vibration.

Fig. 395. Fig. 396.



For continuous working two such extractors are conveniently placed side by side. It is convenient to divide the crude melt into 10 equal parts. Each part—*i.e.*, 88·6 kilos. —is ground up separately, and the lixiviated powder is placed in the extractor. The cover is closed, and water is run in till it runs out at the upper cock. This cock is then closed and steam is turned in. The quantity of liquid is about 3600 litres. When the water boils the supply of steam is so regulated that the manometer shows $1\frac{1}{2}$ to 2 atmospheres. After four hours (altogether) the decoction is passed through the filter-press, and the filtrate is run into a large cistern. The residue is now placed in the second extraction pan, and again treated with 3600 litres in the same manner. This second liquor is now transferred to the first apparatus, which has been already charged with a fresh portion of melt, so that the fresh melt is always extracted with the second extract of the former charge. The doubly extracted residue, a powder resembling humus, forms a part of the poisonous, useless magenta residues.

The colour liquor of one decoction (about 3600 litres) deposits a little impurity on standing for half-an-hour. It is let off into an apparatus placed below, and whilst still hot is stirred up with 200 kilos. of rock-salt. The colouring matter is now converted into a hydrochlorate, and is very completely deposited owing to the presence of salt. The liquid drawn off after two days is collected in a large cistern, and the colouring matter remaining is precipitated from time to time by means of a little milk of lime; it is filtered off and worked up separately. The lye now obtained, containing much arsenious acid, should be completely precipitated with lime to remove the arsenic. This is, unfortunately, often not done at all, or at least very imperfectly, so that the poisonous waters enter the rivers and occasion extraordinary pollution. The lime to be obtained in this manner is of considerable bulk, and forms the second and larger portion of the poisonous residues.

The crude magenta after being salted out has to be purified. Along with several rosanilines—chrysaniline, mauvaniline, violaniline—it contains further constituents not yet understood. The separation of these ingredients depends on a systematic fractional precipitation. The crude magenta from two extractions ($=\frac{1}{5}$ of a melt) is dissolved in a wooden vat in 1000 litres of water boiled by steam. To the boiling water there are added gradually 40 litres of a solution obtained by dissolving 40 kilos. soda-ash in 100 litres water. A part of the colouring matter separates out as a green or golden shining resin on the sides of the vat and on the surface of the liquid. The resin is skimmed off, and the liquid is rapidly poured through a coarse sieve into a wooden butt.

To the filtrate there are added 2 litres hydrochloric acid to prevent the separation of chrysaniline, and to delay the crystallisation of the magenta. There is laid upon the surface of the liquid a cover with a number of wooden rods, by which means the cooling takes place more slowly. When the lid is taken off after the lapse of two days it is found covered with a layer of fine crystals. The lye is run into a cistern, and the crystals adhering to the sides and the bottom are allowed to drop off. These crystals are let dry first in the air, and then in a drying-room at 40°. In this manner 20 kilos. of magenta crystals are obtained, while about 4 kilos. of magenta remain in the mother liquor, and the weight of the resin eliminated is 15 to 16 kilos. The mother liquor from the crystallisation is precipitated with soda-lye, and the coloured base deposited as a brownish-red mud after about 40 kilos. (calculated on the dry matter) have accumulated, is dissolved in hydrochloric acid. This solution is treated exactly as in the purification of the crude magenta liquor; *i.e.*, about $\frac{1}{3}$ of the colouring matter is separated out as resin by the addition of soda-lye; the filtrate on cooling yields a crop of magenta crystals. In this mother liquor there remains very much chrysaniline along with a smaller portion of magenta. By precipitation with soda-lye, filtering and concentrating the base with acetic acid, we obtain *cinnamon brown*.

The resin separated on purifying the crude magenta (resin I.) is dissolved in hydrochloric acid. On boiling the acid liquor a little resin separates out, chiefly *mauvaniline*. By the cautious addition of soda-solution a portion of colouring matter is separated out, and the mother liquor (after filtration and cooling) yields a further quantity of magenta. The mother liquor from this crystallisation is mixed with the resin I. Resin II., obtained on purifying resin I., is dissolved in hydrochloric acid, and the acid liquor is boiled, when some mauvaniline again separates out and is removed. The hot solution is mixed with salt, when cerise is precipitated. It is filtered, and the coloured base, after washing, is neutralised with hydrochloric acid and concentrated by steam in iron pans. It is then the *cerise* of commerce.

In the filtrate from the precipitate of cerise the magenta remaining in solution is precipitated by soda-lye, and the base obtained is mixed with the resin II. remaining from resin I. The more or less complete separation of the bye-products depends on the demands of the market. The required tones of magenta, cerise, cinnamon brown, maroon, &c., are prepared by mixing suitable products. Mauvaniline (along with violaniline) is an almost worthless product, and is very seldom made soluble by treatment with fuming sulphuric acid, but is more frequently neglected.

In order to test a magenta for the presence of chrysaniline a portion is dissolved in hot water. A little hydrochloric acid is added and zinc dust in small portions until the red colour has disappeared. The reduction is promoted by heat. Magenta free from chrysaniline dissolves to a clear, colourless liquid, whilst the presence of chrysaniline gives a more or less distinct yellowness.

The arsenic process is said, as compared with the nitrobenzol process to have the advantage that the quantity of bye-products is considerable enough to render it more profitable. In the meantime the nitrobenzol process yields a very fine maroon, fully equal to that obtained by the arsenical process. Except for the production of acid magenta, that obtained according to the above described process is only suitable for nferior rosaniline blues of a reddish cast. Neither cotton blue nor Nicholson blue can be obtained from it in a satisfactory manner.

Coupier's process for magentas, which has been carried on for years at the colour-works at Hoechst on the Main, at the Berlin Joint Stock Aniline Co., and elsewhere, avoids the use of arsenic acid, and is founded on the oxidising action of nitrobenzol containing nitrotoluol upon aniline oil in presence of iron and hydrochloric acid. An enamelled pan, fitted with an agitator and an outflow pipe, is charged with 38 kilos. aniline oil, 17 to 20 kilos. nitrobenzol, 18 to 22 kilos. hydrochloric acid, and 2 to $2\frac{1}{2}$ kilos.

iron turnings. The pan is heated to 180°, with stirring, for four to five hours. The crude melt, scooped out upon sheet-iron trays with iron ladles, still contains 25 per cent. of aniline. It is dissolved in water, the rosaniline is separated with common salt, and the unconverted aniline is distilled off from the lye after the addition of lime. The formation of this rosaniline (Brüning's red, Coupier red, nitrobenzol red) may be represented by the following equation:

$$2C_7H_7.NH_2 + C_6H_5.NO_2 = C_{20}H_{19}N_3 + 2H_2O.$$

Lange observes that in the nitrobenzol magenta process the nitro compounds have merely an oxidising action, or if they contain methyl groups they participate in the formation of rosaniline in so far only as they furnish the atom of carbon necessary for the production of carbinol.

The salts of rosaniline have mostly in reflected light the green metallic lustre of the elytra of certain beetles (*Cetoniadæ*, &c.), whilst by transmitted light they appear red. The hydrochlorate was formerly called fuchsine, the acetate roseine, and the nitrate azaleine. The salt obtained by the action of mercuric nitrate was called *rubine*. Their solutions in water have the splendid shade well known as magenta.*

Its tinctorial power is very great; 1 kilo. of magenta suffices for 200 kilos. of wool. Aniline tannate is sparingly soluble in water.†

Rosaniline is the basis of most of the other aniline colours; thus blue and violet colouring matters (alkylised rosanilines) may be produced from the rosanilines by partially or entirely replacing the amidohydrogen atoms by alcohol radicles. More recently, however, some of these alkylised rosanilines are preferably obtained by introducing the alkyl (*e.g.*, methylaniline), not into the pre-formed rosaniline, but into the aniline and toluidine, which is then submitted to oxidation for obtaining alkylised rosaniline.

Acid magenta, Rubine S, or acid rubine, consist of mixtures of the sodium or ammonium salts of the pararosaniline and rosaniline trisulpho acids; according to—

$$HO.C\begin{cases}C_6H_3.NH_2.SO_3Na\\C_6H_3.NH_2.SO_3Na\\C_6H_3.NH_2.SO_3Na\end{cases} \text{ and } HO.C\begin{cases}C_6H_2.CH_3.NH_2.SO_3Na\\C_6H_2.CH_3.NH_2.SO_3Na\\C_6H_2.CH_3.NH_2.SO_3Na\end{cases}$$

It is obtained by heating magenta with fuming sulphuric acid to 168° to 170°, pouring into much water, supersaturating with milk of lime, and treating the solution with soda after removing the gypsum. The sodium salt obtained on evaporation is readily soluble in water, and, unlike ordinary magenta, dyes in a strongly acid bath.

Aniline Blue.—If rosaniline is heated with about 10 parts of aniline and a little benzoic acid (the action of which is not yet understood) to the boiling point, ammonia escapes, and the excess of aniline distils over—

$$C_{20}H_{19}N_3 + 3C_6H_5.NH_2 = C_{20}H_{15}(C_6H_5)_3N_3 + 3NH_3.$$

The residue is neutralised with hydrochloric acid; triphenylrosaniline hydrochlorate is insoluble in water (though the excess of aniline dissolves as hydrochlorate), but more readily soluble in spirit (spirit blues).

If, in like manner, aniline is allowed to act upon a mixture of pararosaniline and rosaniline, we obtain a mixture of the hydrochlorates, sulphates or acetates of triphenylrosaniline and triphenylpararosaniline occurring under the trade names of aniline spirit blue, gentian blue, opal blue, and light blue—

* Magenta is soluble in acetic acid, in alcohol, in glycerine, and in solutions of alkaline bicarbonates. By acids the colour is turned more on the blue side, but is apt to be dulled and impoverished.

† Magenta, like many other coal-tar colours, is apt to be sophisticated with sugar and dextrine.

$$C\begin{cases}C_6H_4.NH.C_6H_5\\C_6H_4.NH.C_6H_5\\C_6H_4.N.C_6H_5.HCl\end{cases}\quad\text{and}\quad C\begin{cases}C_6H_3.CH_3.NH.C_6H_5\\C_6H_4.NH.C_6H_5\\C_6H_4.N.C_6H_5.HCl\end{cases}$$

To render aniline blue soluble in water it is treated with concentrated sulphuric acid. The mixture of sodium salts, of triphenylrosaniline, monosulpho acid, and triphenylpararosaniline monosulpho acid, occurs in trade under the names of *Nicholson blue*, *alkali blue*, and *soluble aniline blue*. If it contains also disulpho acids we have—*water blue*, *China blue*, and *marine blue*. If aniline is heated to 250° with aniline hydrochlorate we obtain diphenylamine hydrochlorate $(C_6H_5)_2NH.HCl$. The diphenylamine on heating with oxalic acid to 120°–130° yields triphenylpararosaniline—

$$3(C_6H_5)_2NH + H_2C_2O_4 = C_{19}H_{14}(C_6H_5)_3N_3 + CO + 3N_2O.$$

The hydrochlorate is sold as spirit-*diphenylamine blue*, or *Bavarian blue*, and is distinguished from aniline blue merely by the absence of triphenylrosaniline. When rendered soluble by treatment with concentrated sulphuric acid the sodium salts are sold as *alkali blue D*, and *Bavarian blue D S F*.

According to De Laire and Girard (1866), the mixture of aniline and aniline hydrochlorate is heated in an enamelled cast-iron autoclave for twenty-four hours, at a pressure of 3 to 4 atmospheres and a temperature of 250°. From time to time the ammonia collecting in the autoclave must be expelled by opening a cock, as otherwise the reaction might be reversed, and the yield of diphenylamine might be decreased. In this manner the yield of diphenylamine is 50 per cent. of the weight of the aniline used. The mass taken out of the autoclave is treated with strong hydrochloric acid in order to separate the unchanged aniline from the diphenylamine. From six to ten volumes of water are now added, which occasions a dissociation of the diphenylamine salt into base and acid. The base liberated collects on the surface of the liquid as an oily layer, which, when cold, is taken off, pressed, and distilled. It forms a solid, crystalline, yellowish-white mass, which melts at 50°–55° and distils at 310°. By sulphurising the diphenylamine or its alkylised products, they obtain the mono- and disulpho-acids, which, after treatment with oxidising agents, can be at once used in dyeing and printing for the production of blacks and violets.

For producing alkylised diphenylamine various methods may be adopted—*e.g.*, (*a*) the action of methyl-chloride or nitrate at a temperature below 100°; (*b*) the action of methyl-aniline upon aniline hydrochlorate; (*c*) the action of methyl-alcohol upon anhydrous diphenylamine hydrochlorate; (*d*) the action of the nascent chlorides of the alcohol radicles, *i.e.*, by treating diphenylamine with a mixture of hydrochloric acid and methyl-alcohol, when the most important of these bases, *methyl-diphenylamine :*

$$(C_6H_5)_2NH + C_2H_3Cl = (C_6H_5)_2CH_3N.HCl,$$

is formed. The latter base is obtained by heating 100 kilos. diphenylamine, 68 kilos. hydrochloric acid of sp. gr. 1·2, and 24 kilos. methyl-alcohol, in an enamelled cast-iron autoclave for eight to ten hours in the oil bath at 200° to 350° and bringing the mass in contact with hot caustic soda-lye. The crude base separates out and is purified by distillation. It boils at 282° to 286°; its salts are decomposed by water. If heated to 110° to 120° along with oxalic acid, it becomes a blue. In a quite analogous manner the bases *ethyl-*, *amyl-*, and *benzyl-diphenylamine* may be obtained, which all yield blue colouring matters on treatment with oxidising agents.

For obtaining diphenylamine blue, soluble in water, one part of one of the sulpho-acids of diphenylamine is heated in an autoclave with two parts of oxalic acid, at a temperature not exceeding 130°. After heating from eighteen to twenty hours the mass is let cool, treated with boiling water, saturated with ammonia, filtered; the colouring matter is precipitated with sulphuric acid, washed with acidulated water, and finally converted into the salt desired, with ammonia, soda, or lime. The blue solution is

evaporated to dryness and the residue is pulverised. For silk there is used the ammonium salt, for wool the sodium salt, and for cotton the calcium salt.

Aniline Violet.—If rosaline is heated in an alcoholic solution with methyl chloride or iodide, or ethyl bromide, we obtain the methyl and ethyl derivatives of rosaniline, the hydrochlorates, hydriodates, or acetates of which are known as *Hofmann's violet, iodine violet, dahlia, primula, red violet, violet R.*, &c. The blue violet hydrochlorate of triethylrosaniline corresponds to the formula—

$$C\begin{cases}C_6H_3.CH_3.NH.C_2H_5\\C_6H_4.NH.C_2H_5\\C_6H_4.NH.C_2H_5Cl\end{cases}$$

Methyl Violet or *Paris Violet* is substantially the hydrochlorate of pentamethylpararosaniline—

$$C\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)HCl\end{cases}$$

and is formed by oxidising dimethylaniline with copper chloride, which is first mixed with much sodium chloride, then with dimethylanine and acetic acid and dried at 50°. The bulk of the sodium chloride is removed by means of a little water, the residue is removed with water, the copper is precipitated by hydrogen sulphide, the colouring matter is precipitated with much salt, and purified by re-crystallisation. According to the statement of the Baden Aniline Works, methyl violet is obtained as follows: Into 100 kilos of dimethylaniline 18 or 20 kilos. of chlorocarbonic oxide are introduced at 20°, and after standing for twenty-four hours, 50 more kilos. of dimethylaniline and 30 kilos. of powdered zinc chloride. Then, whilst constantly stirring at 40° to 50° chlorocarbonic oxide is introduced until there is an increase of 20 kilos. in weight. The reaction is completed by heating for six hours to 50°. From the melt obtained the colouring base is extracted in the usual manner by supersaturation with soda lye and distillation with steam, and this base is again converted into a sulphate. From the hot solution of the latter the finely crystalline hydrochlorate of methyl violet may be obtained by an addition of common salt. The same method is taken in obtaining the corresponding violet colours from diethylaniline and methylethylaniline.

A. W. Hofmann gives the following equations for the formation of the colouring matter obtained by the action of phosgene upon dimethyl aniline—

$$C_6H_5N(CH_3)_2 + COCl_2 = C_6H_4N(CH_3)_2COCl + HCl.$$
$$C_6H_4N(CH_3)_2COCl + C_6H_5N(CH_3)_2 = [C_6H_4N(CH_3)_2]_2CO + HCl.$$
$$[C_6H_4N(CH_3)_2]_2CO + COCl_2 = [C_6H_4N(CH_3)_2]_2CCl_2 + CO_2.$$
$$[C_6H_4N(CH_3)_2]_2CCl_2 + C_6H_5N(CH_3)_2 = [C_6H_4N(CH_3)_2]_3CCl + HCl.$$

The hexamethylpararosaniline is sold as a hydrochlorate under the names *crystal violet*, or violet 6B.

Methyl violet is soluble in water; it dyes silk, wool, and cotton prepared with tannin and tartar emetic.

If methyl chloride is heated in an alcoholic solution with benzyl chloride,

$$C_6H_5.CH_2Cl,$$

and soda, a part of the methyl groups are replaced by benzyl and the tone of the colour is turned more to a blue. The hydrochlorate of pentamethylbenzylpararosaniline:

$$C\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_6H_4.N.CH_3.C_6H_5.CH_2Cl\end{cases}$$

is an article of commerce, under the names *Methyl violet 6B*, or *Benzyl violet.*

Aniline Green.—The chlormethylhexamethylpararosaniline hydrochlorate is now very generally preferred to the chlormethylhexamethylrosaniline hydrochlorate, obtained

by the action of methyl chloride or iodide upon rosaniline, the double zinc chlorides of which are met with under the names, iodine-green, night-green, or Metternich green. The double zinc chlorides of the former compound are sold as methyl green, Paris green, or light green. The compositions of both are shown by the formula—

$$C\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2.CH_3Cl\\C_6H_4.N(CH_3)_2Cl + ZnCl_2\end{cases} \qquad C\begin{cases}C_6H_3.CH_3.N(CH_3)_2\\C_6H_4.N(CH_3)_2.CH_3Cl\\C_6H_4.N(CH_3)_2Cl + ZnCl_2\end{cases}$$

Methyl green. Iodine green.

Both dissolve in water, with a blueish-green colour.

The double zinc chloride of bromethylhexamethylpararosaniline, which is sold as *ethyl green*, is obtained by the action of bromethyl upom methyl violet.

The bluish-green sodium salt of tetramethyldibenzylpseudorosaniline disulphoacid is known as *fast green*. The respective compositions of the two colours are—

$$C\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2.C_2H_5Br\\C_6H_4.N(CH_3)_2Cl + ZnCl_2\end{cases} \qquad HO.C\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_2.C_6H_4.SO_3Na)_2\end{cases}$$

Ethyl green. Fast green.

Aniline yellow, along with some other colours prepared from aniline, is discussed among the azo-colours.

Flavaniline, obtained by heating acetanilide with zinc chloride, is no longer an article of commerce. It is included—as is also the *chrysaline* or *phosphine* obtained—as bye-products of the manufacture of magenta, among the quinoline and acridine colours.

Aniline Black is an intense aniline green, produced by the slow oxidation of aniline. It is almost exclusively produced upon the fibre, and more generally in printing than in dyeing, in the strict sense of the word. A black dye which can be obtained in trade and can be conveniently applied both in dyeing and printing does not hitherto exist. The formation of aniline black, however obtained, seems to take place as follows:—

$$\underset{\text{Aniline.}}{nC_6H_5.NH_2} = \underset{\text{Aniline black.}}{n(C_6H_5N)} + nH_2$$

According to R. Kayser, aniline black has the formula $C_{12}H_{10}O_2$; according to Goppelsröder, $C_{24}H_{20}N_4$; according to Nietzki, $C_{30}H_{25}N_5$; and according to Liechti, $C_{18}H_{15}N_3.HCl$.

The formation of aniline black by the action of oxidising agents upon aniline oil is said to have been observed by Fritsche as early as 1843.*

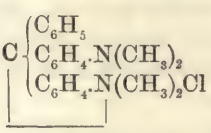
As oxidising agents for obtaining aniline black there are used potassium chlorate and copper chlorate, ammonium ferrocyanide, potassium chromate, and latterly, above all others, ammonium vanadate. One part of the vanadium preparation, in presence of the requisite quantity of potassium chlorate, can convert 1000 parts of aniline hydrochlorate into black. The use of aniline black is confined almost exclusively to cotton printing and dyeing. For woollen dyeing it would be requisite to bring it into a soluble state after the manner of indigo, which has not hitherto been found practicable.

Aniline black has now for some years been used as a marking ink for linen, under the name jetoline.

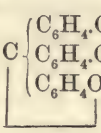
Along with magenta there figure, as representatives of the different classes of triphenylmethan colours,

* The practical discovery of the colour was made by J. Lightfoot in 1863.

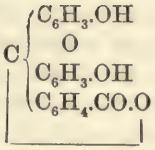
Malachite Green, Rosolic Acid, and Fluoresceine—



Malachite green as Hydrochlorate.



Pararosolic acid.



Fluoresceine.

Benzaldehyd Green or Malachite Green.—This compound was at first obtained on Döbner's process by the action of benzotrichloride upon dimethylaniline and zinc chloride, but it is now prepared universally by the oxidation of the tetramethyl-diamidotriphenylmethan obtained from benzaldehyde with dimethylaniline.

Oil of bitter almonds, or benzaldehyde, is now chiefly obtained by introducing chlorine into toluol, and boiling the benzyl chloride thus produced, $C_6H_5.CH_2Cl$, with copper nitrate and water, or by boiling the benzyl chloride, $C_6H_5.CHCl_2$ (obtained on passing chlorine into boiling toluol), along with milk of lime. *Benzotrichloride*, $C_6H_5.CCl_3$, is obtained by the prolonged treatment of toluol with chlorine.

Dimethylaniline is obtained by heating aniline and soda-lye to 100° and gradually introducing chlormethyl, the pressure not being allowed to rise above 6 atmospheres—

$$C_6H_5.NH_2 + 2CH_3Cl + 2NaOH = C_6H_5.N(CH_3)_2 + 2NaCl - H_2O.$$

Or aniline is heated under pressure with methyl alcohol and hydrochloric acid. According to O. Mühlhäuser, there are placed in an enamelled cast-iron autoclave 60 kilos. aniline oil (for blues), 45 kilos. wood spirit, and finally 18 kilos. hydrochloric acid at 32° Tw. When the apparatus is charged, the entrance is tightly closed, and heat is applied by means of an open coke-fire.

On commencing the reaction at a moderate heat, the pressure in the autoclave quickly rises to 25–28 atmospheres, at which it is kept for four to five hours. At the end of this time the methylation of the aniline is complete, and the autoclave may be let cool. After the lapse of twelve hours the apparatus is still warm and the pressure slight. The contents are brought to the ordinary pressure of the atmosphere by gradually and cautiously raising the filling cover, when a current of methyl chloride escapes. The cover is then unscrewed, and in its place a pipe is introduced for the oil to be forced out. This pipe, which can be screwed in tightly, and which reaches to the bottom of the autoclave, is twofold, and allows on one side admission for compressed air, and on the other an exit for the contents. The warm liquid mass is forced into a wooden tank lined with lead. For decomposing the hydrochlorate and separating the oil, a milk of lime is added, which is prepared the previous day from the lime of 20 kilos. of marble; agitation is kept up during its introduction. The contents of two autoclaves are rendered alkaline in this manner, run into the still, and the cistern is washed out with water. The still is closed, and the oil is expelled by heating over an open fire and the introduction of steam. After heating for two hours the water in the still boils, escapes and is condensed in the refrigerator along with oils which have been carried over. As soon as the distillation of water begins, a current of steam is allowed to enter, and the distillation with the aid of steam is kept up briskly. After the lapse of about five hours the distillation is complete and all the oil has passed over. The operation is then brought to an end by shutting off the steam. The residue in the still is treated as waste; a cock at the bottom allows it to be run off into the drain.

For the separation of oil and water a peculiar receiver is used—a combination of the parting funnel and the Florentine flask. The distillate, which enters the refrigerator in a stream of the thickness of a finger, passes into this receiver, and is separated there into an upper layer of oil and a lower stratum of water. As soon as the level of liquid in the receiver has reached the height of the outflow opening, the water is run off

through a tube, which reaches nearly to the bottom of the receiver. In this manner a preliminary separation of the bulk of the water from the oil is effected. At the end of the distillation a complete separation of oil and water is effected by opening a cock fixed at the lowest part of the bottom. The oil is placed in an iron cylinder along with dry salt in order to remove the last traces of water.

According to Mühlhäuser, the manufacture of malachite green resolves itself into four separate stages—1. The production of a pure, dry leuko-base; 2. The oxidation of this base into green, and obtaining it in a solid form; 3. The purification of the green colouring matter, and the production of the green base; 4. The production of green crystals. To these processes there correspond four independent systems of apparatus in addition to an apparatus for working up the residues. For a daily output of 70 kilos. there are required:

An installation for obtaining the leuko-base, consisting of three cast-iron double pans; connection of the outside pan to the water and steam mains; connection of the cover, fitted with a man-hole and pressure-gauge, with the air-piping from the still, and capable of being heated by direct and indirect steam, as also a worm cooler, and a drying-pan placed beneath the still.

A system of vats for oxidising the leuko-base and obtaining the green in a solid state, consisting of an elevated vat for dissolving the leuko-base; three oxidation butts fitted with agitators; the precipitating vats corresponding to these three oxidising vats, and placed below them, with box filters for previous and subsequent filtration.

The purifying system consists of a horizontal pan provided with an agitator, and containing 3500 litres. This pan has an elevated dome with a man-hole. A second opening of equal size is situate close to the bottom, and serves for emptying the pan, which has a slight incline. This pan is in connection with the water and steam mains, and also with a pressure-filter, a cast-iron chest, the inside bottom of which can be unscrewed. This chest is divided into two compartments by a strong cotton cloth in such a manner that the liquid streaming in from below under pressure allows only dissolved substances to flow into the second compartment, but retains the solids. The filtrate escapes through a side aperture in the chest, and flows through a pipe into the precipitating vats, with three filter-chests placed below.

The system of crystallisation consists of a vat for dissolving the bases, of the capacity of 2000 litres, and six crystallising vats, each of the same size, and provided with round floating covers in several compartments.

For producing the leuko-base there are placed in the double pan, provided with an agitator, 100 kilos. of dimethylaniline and 40 kilos. of benzaldehyde. The mass is kept in agitation, and there are added within two hours 40 kilos. of anhydrous zinc chloride in powder. The pan is closed, and it is heated to 60° the first day, to 80° the second, and to 100° on the third, the water in the outside kettle being brought to a boil. After thus working for three days the condensation is completed, and the leukobase can be separated from the excess of dimethylaniline. A pressure-pipe is placed in the pan, and the contents, yet hot, are forced into the still.

The mass in the still is exposed to the action of direct steam, which carries along with it the oil; the steam and oil are liquefied in the refrigerator and collected in a receiver. The distillation is continued until clean water passes over. By opening the outlet-cock in the vaulted bottom the contents are entirely discharged into a copper pan placed below, and there allowed to cool. The liquid solution of zinc chloride is separated from the supernatant solid base by means of syphons, washing lastly with cold water. The solid base remaining in the copper pan is melted by admitting steam into the outer pan, and dried by agitation, which takes about twelve hours. The dry liquid base is placed upon zinc plates in such a manner that every plate receives a nett weight of 33 kilos.; any residue is weighed into the next operation. The yield

from 100 parts dimethylaniline, 40 benzaldehyde, and 40 solid zinc chloride is about 123 parts.

In order to remove the base from the zinc plates, one plate with its 33 kilos. is placed in a small wooden vat holding 400 litres. The plate is laid upside down upon a steam-worm in the vat provided with many apertures; steam is turned on, and the base is melted off the plate. When this is done the plate is removed; about 200 litres water are run into the vat and heated to a boil, so that the base melts. To the boiling mixture are added 25 kilos. hydrochloric acid at 32° Tw., a quantity which suffices for complete solution. If, on pouring a sample into water, there still remains a white milky turbidity of basic salt, a little more acid is added, until all the test shows complete solution—*i.e.*, a sample poured into water remains clear, and all the leucobase is converted into a bi-acid salt. The clear solution is run into a vat placed below, containing 1000 litres water, and is mixed with 31 kilos. of acetic acid of 40 per cent., with thorough agitation. For obtaining the lead peroxide there are used 67 kilos. litharge, 125 kilos. acetic acid at 40 per cent., and 81 kilos. chloride of lime. The dark-brown paste produced is placed in a cask, and made up to a nett weight of 168 kilos. by the addition of water. The whole is then divided into three small tubs, so that in each tub there are exactly 56 kilos. of paste, corresponding to 33 kilos. of leucobase.

For producing the green there is placed in each of the vats its portion of peroxide paste, which is thoroughly mixed up in five to ten minutes by means of the agitator. The solution is then a deep green.

In order to precipitate the paste in the small dissolving-vat placed above the oxidation-vats, 72 kilos. sodium sulphate are dissolved in 200 litres of water, and made up to a volume of 300 litres. Immediately after the oxidation 100 litres of the solution of sulphate are let run into each of the three oxidising vats with vigorous stirring. The sodium sulphate precipitates all the lead as a sulphate. It is allowed to settle for twelve hours, and filtered the next day into the precipitating-vats through a chest lined with felt.

For precipitating the colouring matter, the green is first converted into the sparingly soluble double zinc salt. As this double zinc chloride is sparingly soluble even in a dilute solution of zinc chloride, it is mixed with an excess of zinc chloride, and then completely salted out with common salt. Into each vat there are stirred in, first, 20 kilos. of zinc chloride, and the double zinc salt is completely salted out by adding 175 kilos. of common salt, which is also stirred in. The precipitation is complete as soon as a drop of the liquid applied with a glass rod to a slip of filter-paper no longer shows a coloured margin. All three vats are treated in the same manner; allowed to stand for twelve hours, and finally passed through a chest-filter. The residue is drained, and consists of a moist mixture of double zinc salt, resin, and excess of salt.

To separate the double zinc salt from the accompanying matters the mass is stirred up with hot water in a large horizontal boiling-pan. For this purpose it is conveyed into 2400 litres of hot water, keeping the agitator in action, boiled for ten minutes, and about 500 litres of cold water are run in to separate out the resin, which at the high temperature had dissolved along with the green. The pan is closed and left at rest for ten minutes. The resin has in the meantime been chiefly deposited and may be filtered off, forcing the liquid through a filter press by means of compressed air. The filtrate runs into a wooden vat, where it is let cool down to 40°, and is then precipitated by stirring in 100 kilos. ammonia.

If the temperature is attended to, we thus reach the precipitation of the base in a melted state, without including the zinc hydroxide, which is completely dissolved. The liquor is filtered into an iron cistern and passed on to the ammonia still; the greyish-white base is packed in bags and drained in the centrifugal. The yield of moist base is 82½ kilos.

Leuko-base.	HCl at 32° Tw.	Acetic Acid 40 per cent.	PbO	Acetic Acid 40 per cent.	Chloride of lime.	Salt cake.	NaCl	$ZnCl_2$	Ammonia.	Yield of moist base.
3×33	3×25	3×31	67	125	81	72	3×175	3×20	100	84.0
3×33	3×25	3×31	67	125	81	72	3×175	3×20	100	85.0
3×33	3×25	2×31	67	125	81	72	3×175	3×20	100	82.5

Along with the green base there is obtained the insoluble residue of double zinc chloride.

For crystallising we dissolve in a wooden vat holding 2000 litres 120 kilos. of oxalic acid in 1200 litres of water, promoting solution by heating to a boil; 100 kilos. of base are then added, which dissolves in the oxalic acid. The volume of the liquid is made up to 1800 litres, and it is filtered into a tall, slightly conical cask, holding 2000 litres. Into the liquid, which has a temperature of 80°, there are stirred 30 kilos. of ammonia at 20 per cent. in a thin stream, and the surface is covered with boards cut to fit, which float upon the liquid and are adapted to the circular form of the cask.

The separation of the crystals ensues, chiefly not at the bottom, but on the sides and on the lid. The crystallisation is broken off as soon as the temperature within the cask has fallen to 18°. If it were allowed to cool down lower, ammonium oxalate would separate out and would contaminate the green in a very unpleasant manner. In order to separate the crystals from the mother liquor the floating boards are removed and a spigot at the bottom is withdrawn. The crystals are left in a felt filter through which the liquid has to pass.

The crystals are first taken away from the bottom, and those on the sides are scraped down. The crystals from the sides and the cover are mixed on a filter, and those from the bottom are kept separate. After drainage on the filters the crystals are packed in woollen bags and drained in centrifugals. The size of the crystals depends on the position of the crystallising vats, and the thickness of the wood-work. The vats should be set in places free from agitations or shocks, such as might be produced from steam engines, pumps, &c., and must be on the firm ground.

The thickness of the wood must not be excessive. If such is the case the crystals are too large and are open to all the defects of large crystals. The crystals after being whizzed are finally uniformly distributed over a fine sieve to prevent them from adhering together, and are dried at 50°–60° in a drying stove. The yield is 70 kilos.

As bye-products are obtained, during the condensation, the oil driven off and a lye containing zinc chloride; from the oxidation, a mixture of lead sulphate and a little colouring matter; on dissolving the crude colouring matter, the double salt of zinc containing resin and adhering colouring matter; on precipitating the base from the solution of the double chloride, a lye containing ammonia; lastly, from the crystallisation, a mother liquor from which oxalic acid and a quantity of good base may be recovered.

About 70 kilos. of "driven-off oil," the yield of 10 lots, are once more distilled with direct steam, separated from water in a cylindrical pan, and dried with anhydrous sodium chloride. The dimethylaniline thus obtained is used in a fresh condensation.

The solution of zinc chloride drawn off from the leuko-base is filtered, and after it has been brought up to 50 per cent. $ZnCl_2$ by the addition of solid zinc chloride, it serves for salting out the green.

The lead residues from ten lots are boiled up in a tub with 2000 litres of water, allowed to settle and filtered when cold. The saline matter liquor is separated by filtration. The double salt remaining on the filter is worked up for green crystals with a succeeding lot. The lead sulphate, after again boiling up with water to which a little sulphuric acid has been added, is filtered and dried, and is used as such.

200 kilos. of moist double zinc chloride residues are stirred into 2000 litres of boiling water and mixed with 20 kilos. of hydrochloric acid. After boiling for 30 minutes it is let settle and filtered into a vat below. From the filtrate the base is separated out with soda. The residue in the boiling vat, consisting of resin and residues of salt, is thrown away. The base separated out by soda is worked up for liquid green or so-called *marine blue.*

The lye containing ammonia is treated for ammonia.

The mother-liquor separated from the crystals is heated to 80° in a vat and mixed with soda-lye until it has a slight alkaline reaction. The green base separates as a dense resin, which incloses but little oxalates. It is allowed to cool, and filtered. The filtrate (sodium oxalate) is mixed with calcium chloride and worked up for calcium oxalate, which is filtered, and after again being boiled in water, and being passed through the filter press, it goes back into work for the recovery of oxalic acid. The resinous base from the mother liquor is boiled out with water, and after separation from the washing water it is converted into green or navy blue.

Production of Liquid Colour.—The base from the mother liquor, or that from working of the double zinc residues, is first mixed with an equal weight of the strongest hydrochloric acid and heated on the water bath in an enamelled pan. The melt obtained is baled into water at 50°, with stirring. Resinous products separate and the green remains in solution. After standing for about a day it is filtered into a tub, in which the base is precipated by ammonia with the aid of heat. The base thus purified serves for the production of colours.

Liquid Green.—50 kilos. of the base just mentioned are dissolved in 40 kilos. of hydrochloric acid and 150 litres water, allowed to cool, and filtered. The filtrate is slightly acidified, if necessary, and made up with distilled water to the tone of a green solution obtained with 20 grammes crystal green in 80 grammes water. This solution is sold as liquid green.

For so-called "navy blue" 50 kilos. of base are dissolved in 40 kilos. of hydrochloric acid and 150 litres of water, and filtered when cold. The filtrate is again heated, and mixed with 22½ kilos. *violet* 3B, which is sprinkled in while stirring, and dissolved. The solution is made up with distilled water to 250 litres and filtered when cold. It is sold under the names *liquid indigo blue* (!), *navy blue*, *cotton blue*, &c.

Malachite green is sold as oxalate, $2C_{23}H_{24}N_2.3C_2H_2O_4$, or as the double zinc chloride, $3C_{23}H_{24}N_2.HCl + 2ZnCl_2 + 2H_2O$, by the names *malachite green*, *bitter almond green*, *Victoria green*, *fast green* and *solid green.* It is soluble in water with a bluish-green colour.

Helvetia green, formed by sulphurising malachite green, has disappeared from the market.

For obtaining *brilliant green*, *emerald green*, *new Victoria green*, the procedure is very similar to that for malachite green. 60 kilos. of diethylaniline are heated with 22 kilos. of benzaldehyde and 32 kilos. of dry oxalic acid. The leukobase is dissolved in hydrochloric acid, acetic acid is added, and it is oxidized with a paste of lead peroxide. After throwing down the lead as sulphate, it is filtered, and the green is obtained from the filtrate in the form of a zinc double salt. It is extracted with ammonia in a large boiling-pan, and from this solution the base is precipitated with ammonia. Into the enamelled pan, set in a water bath, there are put 120 kilos. sulphuric acid and 280 litres of water, and 100 kilos. of base are stirred into the warm mixture. After the base is entirely dissolved the contents of the pan are cooled down to 20°, and 130 kilos. ammonia are let run in, in a thin stream and with constant stirring. The solution is heated to 55°–60° until there is a slight separation of green, which may be easily seen if a drop is placed upon a piece of white filter-paper. As soon as a separation appears it is allowed to settle and filtered through felt into a second pan, in which the filtrate is

rapidly heated to 85°–90°. The colouring matter separates out in crystals of a metallic lustre. They are placed on a filter, drained, and freed from mother liquor by whizzing in the centrifugal. The yield is 94 kilos.

The colouring matter consists of the tetraethyldiparaamidotriphenylcarbinol sulphate (rarely the oxalate):

$$C\begin{cases}C_6H_5\\C_6H_4.N(C_2H_5)_2\\C_6H_4.N(C_2H_5).SO_4H\end{cases}$$

The hydrochlorate of tetramethyldiamidodichlorotriphenylcarbinol is sold as *Victoria green* 3B:

$$C\begin{cases}C_6H_3Cl_2\\C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2Cl\end{cases}$$

All these colouring matters dye silk, wool, and cottons, mordanted with tannin and tartar-emetic, a green. But brilliant green has a yellower and Victoria green a more blue tone than malachite green. In wool-dyeing acid green is chiefly used.

Acid green and light green SF is the sodium salt of diethyldibenzyldiamidotriphenyl carbinoltrisulpho acid:

$$HO.C\begin{cases}C_6H_4.SO_3Na\\C_6H_4.N.C_2H_5.CH_2.C_6H_4.SO_3Na\\C_6H_4.N.C_2H_5.CH_2.C_6H_4.SO_3Na\end{cases}$$

According to Mühlhäuser the formation of the leuko-base of acid green is effected by the condensation of 1 mol. benzaldehyde and 2 mols. ethylbenzylaniline by anhydrous oxalic acid according to the equation:

$$C\begin{cases}C_6H_5\\O\\H\end{cases} + \begin{cases}H.C_6H_4.N.C_2H_5.CH_2.C_6H_5\\H.C_6H_4.N.C_2H_5.CH_2.C_6H_5\end{cases} = H_2O + C\begin{cases}C_6H_5\\C_6H_4.N.C_2H_5.CH_2.C_6H_5\\C_6H_4.N.C_2H_5.CH_2.C_6H_5\\H\end{cases}$$

By sulphurising the leuko-base thus formed with fuming sulphuric acid there is obtained a mixture of the di- and tri-sulpho acids of diethyldibenzyltriphenylmethan:

$$C_{37}H_{38}N_2 + 2SO_4H_2 = C_{37}H_{36}(SO_3H)_2N_2 + 2H_2O$$
$$C_{37}H_{38}N_2 + 3SO_4H_2 = C_{37}H_{35}(SO_3H)_3N_2 + 3H_2O.$$

The oxidation of the acid effected with lead peroxide leads to a green colouring matter according to the equation:

$$C_{37}H_{36}(SO_3H)_2N_2 + PbO_2 = C_{37}H_{34}(SO_3)_2PbN_2 + H_2O,$$

which is converted into a sodium salt.

For producing the leuko-base there are introduced 21 kilos. benzaldehyde and 80 kilos. benzylethylaniline into an enamelled double pan fitted with an agitator and connected with the steam and water-pipes. To the mixture, which is kept in motion, there are added 34 kilos. of well-dried and finely sifted oxalic acid. This addition is made in successive portions within an hour. When the mixture is complete the pan is closed, the water in the jacket is brought to 60°, a temperature which is maintained for one day. The two following days the heat is kept at 80°, and on the fourth day it is maintained at 100°. By keeping the given temperature for these times, and agitating continually, the reaction is kept up very regularly. At the end of the fourth day the leuko-base is obtained as a soft green paste, still containing benzoic acid and benzaldehyde. The cover of the manhole is removed and the hot paste is neutralised by agitation with soda-lye. About 100 kilos. of lye at 62° Tw. are needed.

The man-hole is closed, the pressure-pipe fixed in its place, and the contents of the pan are entirely forced over into the still, where the excess of benzaldehyde is completely removed from the leuko-base by distillation in a current of steam. When this

has been effected the still is closed and the contents are heated to a boil with indirect steam. Direct steam is then turned into the boiling mass, which carries with it the benzaldehyde which has escaped the reaction. The distillation is kept up until only clean water passes over, thus showing that the benzaldehyde has been completely separated from the base. The wide cock at the bottom of the pan allows it to be emptied into a double pan placed below. When cold the faintly alkaline lye is drawn off with a syphon from the solidified leuko-base, which is then again washed with water. The liquor and the washings are worked up as sodium oxalate.

The base remaining in the copper pan is melted and heated for about a day, stirring until it is completely dry. When cold the base is broken out of the double pan, and divided as finely as possible by beating with a wooden mallet. The yield is 93 kilos. The condition for producing a good base is pure material—pure benzaldehyde, pure benzol-ethyl aniline, and perfectly dry oxalic acid.

For sulphurising, 200 kilos. of a 20 per cent. fuming sulphuric acid are placed in a pan, fitted up in the same manner as for obtaining the leuko-base. There are then added, with constant stirring, 50 kilos. of the pulverised leuko-base, not letting the temperature rise above 45°, which is effected by a rapid current of water through the jacket. The base soon dissolves in the acid, with an escape of sulphurous and carbonic acids. After the introduction of the leuko-base the pan is heated to 80°–85°, neither higher nor lower.

Specimens taken out of the pan, which may be drawn after two hours of action, are covered with distilled water in a test-tube, and mixed with ammonia in excess, and show the progress and the end of the sulphurising. As soon as such a specimen, after the addition of the ammonia, no longer appears turbid, it is tested in the dye-house against the standard sample, and the process is stopped or continued according as the right tone has been reached or not.

The perfectly sulphurised mass is let cool, and the next day it is forced over into a vat with 1000 litres water. To separate the sulphuric acid it is mixed with milk of lime—prepared from 150 kilos. of lime—until the reaction is slightly alkaline. The mass is heated with direct steam to the boiling-point. To separate out the gypsum in a crystalline state, about 500 litres of cold water are added with agitation, bringing the temperature to 60°–65°. The whole contents are let off into the montejus and filtered through a filter-press. The filtrate is run into a large iron tank containing a copper steam-worm. The cakes remaining in the press are thrown each time into the lime-cask, and after all the residues have been united they are boiled up with 1000 litres of water, and further treated as above. The final residue is thrown away; the filtrates, united, are evaporated down to 1200 litres, and filtered through an open filter into the oxidation-vat set below, where the liquid is cooled to 19°–20°.

For obtaining the lead peroxide needful for oxidation 22 kilos. of litharge are dissolved in 40 kilos. of acetic acid at 40 per cent. and 100 litres of water in a wooden vat, with agitation, and the introduction of steam. The lead acetate thus obtained is mixed with a finely strained paste of chloride of lime (obtained from 27 kilos. chloride of lime and 54 litres water) until all the lead acetate has been converted into peroxide. The end of the reaction is known as follows:—A drop of the lead solution placed with a glass rod upon a slip of filter-paper gives a brown spot of peroxide with a moist colourless spot around it. If this colourless zone is turned yellow on applying to it a drop of a clear solution of chloride of lime, more chloride of lime must be added.

The lead peroxide is allowed to settle, and the weak acetic solution is poured through a filter. After twice boiling up in water and letting settle, the dark-brown mud is placed on a filter; the paste, when well washed, is put in a small tared tub, and the whole is made up with water to a net weight of 56 kilos.

For producing acid green the oxidation is conducted below 20°, the agitator is set in

rapid action, and the mass is acidified with 10 kilos. sulphuric acid at 158° Tw. The lead peroxide is added to the liquid, which is in rapid motion. The colourless solution becomes a deep green, acid green being formed.

After stirring for ten minutes, all the lead and lime are removed from the solution by scattering in about 25 kilos. of soda. The addition of soda must cease as soon as a specimen, after filtration and dilution with water, no longer gives a precipitate on the further addition of soda. It is then heated to 70°, the mass is run off into the montejus and forced through a filter-press with double filter-cloths. The filtrate is passed into an iron cistern fitted with a steam-worm. The green solution is concentrated to about 600 litres and run into the copper stirring-pans placed below, fitted with mechanical scrapers. Here it is evaporated down to dryness, and the residue is exposed for two to three days on zinc plates in the drying-room.

The dried green is ground in a ball-mill (such as used for grinding indigo), and is sent out as a dark green powder. It is also sold in a liquid state—*liquid acid green*—in 10 or 20 per cent. solutions. The yield is 85·5 kilos.

Resorcine, $C_6H_4(OH)_2$, is obtained by melting sodium benzoldisulphate with sodium hydrate.

Into a double pan fitted with an agitator are put 300 kilos. sulphuric acid at 158° Tw. and 60 kilos. of benzol free from thiophene. The pan is then connected with a reflux-condenser. The reaction is set up by constant stirring, supported by the introduction of steam into the jacket, so that the tube connecting the pan and the condenser is but slightly warm to the hand. The vapours of benzol are liquified and flow back. After continuous mixing for about ten hours at a moderate heat the reaction is completed with the formation of benzolmonosulpho acid, $C_6H_5.SO_2.OH$. This acid, dissolved in an excess of sulphuric acid, is put the next day into a pan fixed in an oil-bath (provided with an agitator and connected with a leaden ascending condenser), in order to be converted into the disulpho acid. For this purpose the mass is mixed with 85 kilos. of salt-cake, ground and well dried; the agitator is set in motion, and the oil-bath is heated to 240°. After heating for four hours, the contents of the pan take a temperature of 225°. This heat is kept up for about eight hours, whilst the agitator is in constant action. During the first half of the time benzol distils over and is collected in a receiver, whilst sulphurous acid escapes.

The next day the contents of the pan, which are still moderately warm, are mixed with 1500 litres of water in a wooden vat holding 3000 litres, and limed out with milk of lime made from 200 kilos. of lime, and passed through a sieve. The boiling faintly alkaline mass is chilled with 800 litres of cold water to form gypsum. The contents of the vat are run off into a montejus and forced through the filter-press. The filtrate is led into a large evaporating trough. The press-cakes are again boiled up with about 1500 litres of water, and separated from gypsum after the vat has been filled with water. The combined filtrates are concentrated to 2000 litres, and the solution is then run off into the conversion tanks. An addition of 6 to 10 kilos. of soda is sufficient to precipitate all the lime. The liquor let off into a montejus is separated from calcium carbonate by means of the filter-press. The filtrate is evaporated in two stirring-pans until the scrapers stop from the toughness of the mass. The moist salt is put in flat double pans and dried, constantly stirring with an iron rod, to a powder, which is then ground and sifted. The yield is 200 kilos. sodium benzoldisulphate, $C_6H_4(SO_3.Na)_2$. The following conspectus shows the limit values for so-called "return oil," and yield in two lots:—

Sulphuric acid.	Benzol.	Salt-cake.	Lime.	Soda.	Return Oil.	Yield.
300 ...	60 ...	85 ...	200 ...	6·5 ...	14 ...	180
300 ...	60 ...	85 ...	210 ...	9·0 ...	8 ...	200

There are put 250 kilos. solid caustic soda into an open melting-pan over an open

fire, provided with an agitator, and to effect a more rapid solution there are added 10 kilos. of water. The formation of a scum on the top shows that the caustic is not hot enough to take up the salts to be added without solidifying. It is therefore heated until both the scum and the crusts adhering to the sides are perfectly liquified. If a piece of the salt thrown in melts quickly with a hissing sound the temperature is high enough. The agitator is set in motion, and in a short time 125 kilos. of the dry salt are thrown in, but so that the contents do not boil over, which is regulated by stopping or turning the agitator. The introduction of the salt takes thirty minutes. The mass begins to froth as water escapes; gradually it becomes more quiet, turns oily, and retains a white foam. In time it becomes yellow, and then brown, and spirts violently. When the brown mass no longer works it is ready, and the hot mass is baled out with iron ladles upon iron sheets, where it cools. The process may be explained by the following equation—

$$C_6H_4(SO_3Na)_2 + 4NaOH = C_6H_4(ONa)_2 + 2Na_2SO_3 + 2H_2O$$

The melt, broken up, is thrown into a large stone trough containing 500 litres of water. 9 to 10 carboys of strong hydrochloric acid expel all the sulphurous acid, and produce a moderately acid solution of resorcine. So much acid is added as to turn a piece of blue litmus paper slightly red.

The liquid, run off into an iron receiver lined with lead, is pressed over by opening an air-cock into a horizontal mixing-pan provided with an agitator. In this apparatus the solution containing resorcine is extracted four times, each time with 100 litres of purified amylic alcohol. The solution and the amylic alcohol are mixed for half-an-hour, and the liquid is then syphoned into the elevated pointed cylinder. After settling for an hour the salt solution is run back into the mixer, and the deep brown alcohol charged with resorcine is let into the amyl-cistern. After this extraction has been repeated four times the salt solution is exhausted, and the fourth extract is scarcely coloured. The combined extracts, after standing for twelve hours and separation from the adhering saline solution, are run off into the still.

The amylic solution of resorcine is heated by indirect steam to about 100°. As soon as this temperature is reached direct steam is allowed to enter, which carries away the amylic alcohol, and leaves the resorcine behind in the pan. When only water issues from the condenser the distillation is stopped, and the solution of resorcine is run out into an enamelled iron pan. The water is evaporated off, which takes twelve hours. The resorcine has now to be purified.

The purification is effected by distillation in a vacuum. For this purpose the liquid contents of the double pan (about 30 kilos.) are baled into a copper pan provided with a thermometer, and closed. A copper Liebig's condenser connected with the cover conveys the distillate into a copper receiver with an exit cock, which is again connected with the suction pump. At first some water and phenol pass over from the heated mass, and escape on opening the cock of the receiver. At about 190° the cock is closed, and the pressure of the air is reduced to 630 millimetres. On raising the heat the resorcine begins to boil and passes over into the receiver. Here caution is needed on account of a possible stoppage of the cooler, which, however, may be overcome by letting only a moderate stream of water into the cooling tube, or interrupting it for a time entirely. The liquid resorcine collecting in the receiver is run in known quantities into moulds of tinned copper, and thus the commercial product is obtained of 20 to 23 kilos. of pure resorcine from 125 kilos. of benzol disulphate.

Fluoresceine Colouring Matters.—The halogenous and nitro-halogenous derivations of fluoresceine are colouring matters highly valued as **eosines** (Ἠως, morning redness), surpassing all other colours in lustre and fire. The most important are:

1. *Tetrabrom fluoresceine*, the sodium and ammonium salts of which are met with in trade as eosine, eosine B, soluble eosine, &c., in the form of red and reddish-brown

powders. It is obtained by bromising fluoresceine in alcohol or in water. The garnet-red crystals of tetrabrom fluoresceine sodium (*Eosine A extra*) are used in silk-dyeing, whilst the first-named eosine brands serve especially also in colouring paper and in the manufacture of lakes.

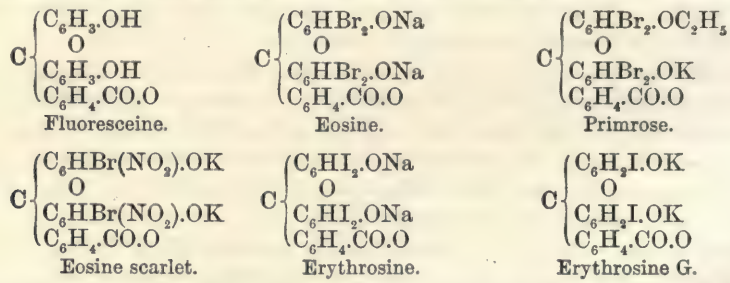
2. *Dibromfluoresceine* occurs in trade as a sodium salt, more or less mixed with tetrabrom fluoresceine under the name of *Eosine orange*.

3. *Ethyltetrabromfluoresceine* is obtained as a potassium salt in red crystals with a green surface lustre. It is known by the trade names primrose, spirit eosine, ethyl-eosine, eosine S., rose J. B. à l'alcool, &c. It is obtained by bromising fluoresceine in hot alcohol, when alkylising and bromising are effected simultaneously. It is used to some extent in silk-dyeing.

4. *Dibromdinitrofluoresceine* is prepared on the large scale by bromising dinitro-fluoresceine in an alcoholic solution, or by nitrising tetrabrom fluoresceine in glacial acetic acid, or by nitrising bibromeosine in a water solution. It is sold under the names: eosine scarlet, eosine B.N., safrosine, lutecienne, daphnine, rose des Alpes, in the state of alkaline salts. The sodium and potassium salts appear black, and the ammonium salt red. These salts meet with but slight application in dyeing, but the ammonium salt and the neutral sodium salt, which when evaporated down in thin layers has a greenish colour, are exported to China to a considerable extent.

5. *Tetraiodofluoresceine* is obtained by iodising fluoresceine in an aqueous solution. Its alkaline salts are of a brown red, but the ammonium salt is of a light brick red. These salts are used in silk and cotton dyeing and paper-staining, under the names erythrosine, eosine J, pyrosine B, iodeosine B, dianthine B, rose B *à l'eau*, soluble primrose, *eosine bleuâtre*.

6. *Di-iodofluoresceine* is also found mixed with tetraiodofluoresceine in the state of an alkaline salt, as erythrosine G, dianthine G, iodeosine G, &c.



Fluoresceine is obtained, according to Mühlhäuser, by melting 25 kilos. of resorcine in a pan placed in an oil bath at 160°, and stirring in 17½ kilos. of phthalic anhydride. The reaction begins as soon as the liquid has been heated for about ninety minutes to 180°. During the reaction, which lasts forty minutes, the mass must not be stirred, as it would otherwise flow over. The mass thickens to a paste, and it is then stirred from time to time by means of an iron rod until it is perfectly dry, which is effected in twenty-four to thirty hours' heating to 200° to 205°. The end of the reaction is observed by the brittleness of a small lump of fluoresceine when struck with the hammer.

The main points to be observed in melting are pure materials and the maintenance of a temperature of 180° during the reaction. If the mass rises during the reaction, and there is danger of an overflow, the temperature is reduced by blowing in air with bellows. The yield of crude fluoresceine is 37½ kilos.

The crude fluoresceine is dissolved by boiling with 500 litres of water and 50 kilos. of soda-lye at 62° Tw., and the liquid is made up to 1000 litres. After filtration into a vat fixed below, the reddish-yellow filtrate is precipitated with 90 kilos. of

hydrochloric acid. The fluoresceine goes down, and the fluorescent colour liquor is poured off. By again boiling up the sediment in 500 litres of water we obtain a reddish yellow turbid liquid, from which the fluoresceine is generally completely precipitated by the addition of a little hydrochloric acid. It is allowed to settle, the solution is decanted off, all the fluoresceine is collected upon a filter, drained, and dried.

The drying is effected in shallow enamelled capsules, the flat bottom of which is about 80 square centimetres; four such capsules are placed on a water-bath, and are then exposed to a temperature not exceeding 98°. At this temperature the moist fluoresceine, which has been spread in a layer of about 5 millimetres in thickness, quickly dries to a fine powder, which is then sifted. The yield is 36 kilos.:

Resorcine.		Phthalic Acid.		$ZnCl_2$.		Crude Melt.		Lye, 62° Tw.		Hydrochloric Acid.
25	...	17	...	8	...	45	...	60	...	100

For obtaining tetrabrom fluoresceine in an aqueous solution, 60 kilos. of soda-lye at 62° Tw. are mixed in a jacketed cast-iron pan with 150 litres of water. Then, whilst the lye is being stirred, 32 kilos. of bromine are run in direct from the bottles by means of a syphon.

Then is formed a mixture of NaBr, $NaBrO_3$, and NaBrO; the last compound is converted into NaBr by boiling for half an hour. The decomposition of the sodium hypobromite is necessary, as otherwise a yellow product would be formed on decomposing with hydrochloric acid.

Meanwhile, in an adjacent steam-pan, 10 kilos. of fluoresceine have been dissolved in 25 kilos. lye at 62° Tw. and 150 litres of water by boiling for thirty minutes. Both solutions are run off into a vat as soon as cold, well stirred up, and precipitated by the immediate addition of 140 kilos. crude hydrochloric acid, with thorough agitation. Yellow bromeosine separates out. It is heated to boiling by direct steam, and as soon as it boils the vat is filled up with water, allowed to settle, the sediment boiled up twice in the same manner with fresh water, and lastly filtered. The eosic acid, thus entirely freed from mineral acids, is dried upon plates, as described under fluoresceine. The yield of tetrabromfluoresceine is 30 kilos.:

Fluoresceine.		Soda-lye, 62° Tw.		Bromine.		Soda-lye at 62° Tw.		Hydrochloric Acid.
16	...	25	...	32	...	60	...	140

Two such lots—*i.e.*, 60 kilos.— of eosic acid are made soluble by means of alcoholic soda in order to obtain *eosine B*, and allowed to crystallise from the solution.

In order to render the eosic acid soluble, we must first ascertain by a trial what quantity of soda is necessary for the formation of the neutral eosine salt. For this purpose we take an average sample of 50 grammes eosic acid, mix it in a litre flask with 175 grammes of alcohol at 96°, and heat to boiling. In the meantime a portion of the soda-lye, to be used on the large scale (1 part sodium hydroxide and 2 parts water = 72° Tw.), and about 40 grammes, are placed in a dropping-bottle.

This bottle with the soda weighs (say) 134·7 grammes. Soda is then let flow in, drop by drop, to the boiling alcoholic solution of eosine. As the soda is added there is formed the red acid salt of eosine, which subsides. This sparingly soluble salt serves as an indicator, for we continue dropping in the soda, keeping up a moderate heat and shaking the flask, until the acid salt dissolves, passing into the neutral salt. The addition of lye must cease as soon as the last granule of eosine sodium has disappeared. The liquid appears now of a yellowish-red, but if an excess of soda has been used it looks blackish-red. Whether the right quantity of soda has been used may be known not merely from the disappearance of the acid salt, but by dipping a glass rod into the solution and letting it dry in the air. If it is then dipped into distilled water, the adhering eosine will dissolve clear if sufficient soda has been added, but if the quantity has been deficient there is formed a cloud round the end of the rod.

A correctly neutralised sample when dropped into a glass of water gives a yellowish-

green dichroism; a solution supersaturated with alkali gives a dirty green colour with a brownish-green dichroism. If the eosine solution is poured into a capsule the margin should look yellowish-red and not brown. In the latter case too much alkali has been added. If the contents of the capsule are allowed to crystallise overnight, there must be no acid salt at the bottom of the cake. On weighing the dropping-flask it came to 114·46 grammes, consequently 20·24 grammes soda had been used to saturate 50 grammes eosic acid. This number is used in calculating the quantity of soda to be employed on the large scale.

Sixty kilos. of eosic acid are placed in a copper pan on the water-bath, and 210 kilos. of alcohol are added—*i.e.*, the quantity which is necessary to keep in solution the salt formed on neutralising the eosic acid with soda. For this purpose there are required $3\frac{1}{2}$ times the quantity of alcohol referred to the weight of the free eosic acid. It is convenient to put the alcohol first in the copper pan, and then to stir in the eosine, which is otherwise apt to adhere to the bottom and is difficult to remove. The water-bath is heated to boiling and the contents of the pan to 60°. When this temperature has been reached we run in $(20{\cdot}4 \times 60) : 50 = 24\frac{1}{2}$ kilos. soda-lye during ten minutes, stirring constantly. The free acid dissolves, after having formed the acid salt. The solution is run into three wooden casks, holding each 120 litres. On the surface of the liquid there are laid thick wooden lids, which dip 1 to 2 centimetres into the alcohol, so as to give the greatest possible space for crystallisation and at the same time to decrease the proportion of the crystals forming at the bottom. The crystals deposited on the cover and the sides are always a finer and better-looking article than those attached to the bottom.

After standing two or three days in a cool place the crystallisation is complete. The cover is raised, the mother liquor run off, and the crystals from the cover and sides are put upon the filter, as are those also from the bottom separately. Cakes of crystals are detached from the wood with a knife. The crystals, when they have been drained, are dried on frames at 60° in the drying-room, which takes three days. When dry the crystals are ground. The brownish-red powder is sold as eosine B:

Eosine.		Alcohol.		Soda.		Eosine B.
60	...	210	...	24·5	...	57·5

The mother liquor obtained on the crystallisation of eosine B is distilled, and yields alcohol at 96 per cent., the colouring matter remaining in solution being disregarded.

The bromising of fluoresceine in an alcoholic solution is effected in three enamelled pans. Each pan is charged with 10 kilos. fluoresceine and 80 kilos. of alcohol at 96°. The bromising is effected by letting 24 of bromine flow in a slow stream and with constant stirring from a bottle fitted with a cock, the exit pipe of which plunges a little into the alcohol. This operation lasts fifteen minutes; when it is completed the mixture is well stirred and covered up. It is set aside four days, but is well stirred up three times each day, thus effecting a complete separation of the eosic acid. In bromising we remark that when half the bromine has been added, the liquor, which was at first a reddish-brown, has changed to a blackish-brown; there is first formed the dibromide of fluoresceine, which is readily soluble in alcohol. On the further addition of bromine the tetrabromide is deposited as a brick-red mass. After standing for four days the alcohol is drawn off with a syphon, and the red deposit is twice washed with alcohol. For this purpose 40 kilos. of alcohol are placed in each pan; it is well stirred up, let stand for one day, and the washing alcohol is then drawn off. A second washing is executed in the same manner. The red deposit at the bottom of the pan is collected upon filters of felt, drained, and pressed. The comminuted press-cakes are dried upon cotton cloths spread out on frames in the drying-room, which lasts two days. The yield of eosic acid is 50 kilos.

The conversion of tetrabromfluoresceine into *eosine A extra* is effected by crystallisation according to the method above mentioned. The crystals are not broken, but merely crushed with a piece of wood to fragments of the size of a nut, and they are despatched in this state. The yield is 50 kilos.

Fluoresceine.		Alcohol.		Bromine.
30	...	240	...	72

Washing Alcohol.		Yield of Eosic Acid.		Soda.		Alcohol.		Eosine A extra.
240	...	50	...	20	...	175	...	50

For obtaining *eosine B* with a red surface, 30 kilos. of tetrabrom fluoresceine, obtained by the alcohol process and finely sifted, are used. The eosine is made soluble in an upright wooden box, which can be tightly closed with a door. In this box are inserted thirty frames, arranged like drawers, each 3 centimetres in height, and with linen bottoms of 6 square metres in surface, at intervals of 3 centimetres, so that one frame is exactly upon the other. The available linen surface extended in the box is about 18 square metres. Upon each frame there is spread as uniformly as possible about 1 kilo. of eosic acid, and after all the frames have been inserted the box is closed. The box is connected with an apparatus for generating ammonia, consisting of a still and two gas-desiccators. The ammonia is conducted into the bottom of the box, it traverses the entire layer of eosine from below upwards, and is very eagerly absorbed by the free eosic acid, in accordance with the equation:

$$C_{20}H_8Br_4O_5 + 2NH_3 = C_{20}H_6Br_4O_5.(NH_4)_2.$$

In about two hours all the eosic acid is converted into the neutral ammonium salt. If a fragment taken out of one of the frames dissolves in distilled water without turbidity, the process is broken off. The slight excess of ammonia escapes into the chimney through an iron tube fixed above the box:

Eosic acid.		Sal-ammoniac.		Lime.	Eosine B.
30·0	...	15·0	...	30	31·8

Utilisation of the Residues.—The alcohol which has been used for bromising in one process is poured into an enamelled pan. It contains free eosic acid, resin, hydrogen bromide, and a little bromethyl. In order to separate the eosine from the alcohol, water is run into the liquid in a thin stream and with constant agitation, about equal to one-third of the volume of the alcoholic solution. If more water is added, the resin is separated out along with the eosine, which has to be avoided. The free eosine subsides to the bottom. After completely settling, the watery alcohol is drawn off. The deposit put on the filter is twice washed with water. If on the second washing the eosine remains suspended for a long time, it is a sign that all the acid is washed out, for in acid water the subsidence is more rapid and without turbidity. If the residue, thus filtered and freed from acid, is sandy, it is, after draining, put through the filter-press and dried; if it is resinous, it must be washed with alcohol to take up the resin. The residuary eosine thus obtained is collected until about 60 kilos. have accumulated. Such residues are then, according to their purity, washed once or twice with alcohol. To each kilo. of eosine residues, we add 2 kilos. of alcohol. The eosine in washing must be ground into the alcohol, if this is neglected and the whole mass is added at once, it clots together and is very difficult to wash.

The eosine after being thus washed is now fairly pure, and is filtered, pressed, and dried. By crystallisation it is made to yield a fine, pure colouring matter. The necessary quantity of soda for solution is determined, and the product is crystallised from alcohol as described above. Many impurities pass into the alcohol. The crystals are dissolved in water, precipitated with hydrochloric acid, filtered, dried and re-crystallised, and then generally yield a product equal in its properties to eosine B.

On working up the alcoholic bromine lye we obtain eosine B, dilute bromising

alcohol, washing alcohol, and mother liquors from the first and second crystallisation. All the alcoholic liquids are collected and redistilled.

The mother liquors obtained from the crystallisation of "Eosine A extra" are separated from alcohol in the distillatory apparatus, and the residue is dried. Here also about 60 kilos. of residues are allowed to accumulate, dissolved in water, and the eosine is precipitated with hydrochloric acid. The further treatment of the dried eosic acid is effected by washing and recrystallisation with alcoholic soda in the manner described above.

The subjoined table (p. 553) collates the conversion of fluoresceine to eosine and the treatment of the alcoholic residues.

For the production of dibromfluoresceine 10 kilos. of fluoresceine are suspended in 80 kilos. of alcohol at 96°, and treated with 12 kilos. of bromine as above described. The fluoresceine passes into solution with the formation of dibromide. When cold the dibromfluoresceine is precipitated with 100 litres water and the diluted alcohol is drawn off. The dibromfluoresceine, separated out as a resin, after washing with water, is dissolved in a cask in 200 litres of water and 20 kilos. lye at 62° Tw., and when cold it is precipitated with 40 kilos. of hydrochloric acid. It is obtained as a pulverulent precipitate, which is freed from acid, filtered, and dried. The yield is 15·4 kilos.

Eosine Orange.—A laboratory experiment shows the quantity of lye necessary for dissolving. To the dibromeosine suspended in 150 litres of hot distilled water there is added the quantity of lye determined by experiment, and the mixture is evaporated to a paste. It is then completely dried on sheet metal in the drying-room. The yield is 17 kilos.

To obtain ethyltetrabromfluoresceine, 80 kilos. of alcohol at 96°, and 20 kilos. of fluoresceine are placed in a jacketed and enamelled autoclave, agitating all the time. The autoclave, which is fitted with an enamelled mechanical agitator and an ascending leaden cohobater, is closed and heated. Steam is let enter the jacket until the alcohol boils. Meantime, 13 kilos. bromine are weighed into a glass bottle provided with a cock, and the bottle is placed upon the elevated refrigerating tub. When the alcohol boils the cock of the bottle is opened and the bromine is allowed to flow down through a glass tube dipping but little into the apparatus, which is connected with the outside air merely by the leaden worm. In this manner four bottles of bromine of 13 kilos. each are successively run in during 50 minutes. The autoclave is then closed as tightly as possible and heated at the pressure of 1 atmosphere; the steam is then shut off, and the mass is left at this pressure for three hours, allowing steam to enter the jacket from time to time. When completely cold the autoclave is opened by raising the lid. The alcohol is drawn off, and the residue at the bottom is placed upon an asbestos filter.

The eosine thus obtained has in this state a black, a greenish-black, or a brown colour. By hot bromising we obtain a mixture consisting chiefly of ethyltetrabromfluoresceine and a little tetrabromfluoresceine. A bye-product is the bromising alcohol containing ethyl and vinyl bromide which is used for eosine B, and alcohol at 96°.

The eosic acid, after draining on the asbestos filter, is pressed and washed with 100 kilos. of spirit in an enamelled pan, distributed in the alcohol with a wooden stirrer, allowed to subside, filtered, and pressed. The filtration residue is again washed with about 100 litres of water. The moist, brown, eosine mass is filtered, pressed, and dried on frames in the drying-room. The yield is 27 kilos. of eosic acid.

Spirit Eosine.—To isolate eosic acid and to render it alcoholic it is crystallised from an alcoholic solution of potassa. The eosine soluble in water remains dissolved in the mother liquor, whilst the spirit-eosine crystallises from the 36 per cent. alcohol.

In order to ascertain the quantity of potassa lye which will be necessary for neutralising the acid, 50 grammes of eosic acid are weighed out, suspended in a glass flask in a mixture of 125 grammes water and 75 grammes alcohol, and heated to boiling. To

Eosic acid	*Eosine A extra*							Eosine A extra.	
	Motherliquor (distilled)	Alcohol (90 per cent. neutral)			Alcohol, 90 per cent.				
		Crude sodium cosate, precipitated with HCl	Washing alcohol (90 per cent.)			Washing alcohol, 90 per cent.			
			Crude eosine crystallised with NaOH	Mother liquor			Mother liquor alcohol, 85 per cent.		
				Crude sodium cosate precipitated with HCl, and crystallised with alcoholic NaOH	Mother liquor, 85 per cent.		Idem.		
					Eosine B			Eosine B.	
Alcohol for bromising.	Acid alcohol				Acid alcohol.				
	Crude eosine washed with alcohol	Washing alcohol				Washing alcohol, 90 per cent.			
		Crude eosine crystallised with NaOH	Mother liquor				85 per cent.		
				Crude sodium cosate precipitated with HCl, and crystallised with alcoholic NaOH	Mother liquor		85 per cent.		
					Eosine B			Eosine B.	
Washing alcohol						Washing alcohol, 90 per cent.			
Products					Acid alcohol.	Washing alcohol, 90 per cent.	Mother liquor alcohol, 85 per cent.	Eosine B.	Eosine A extra.

the boiling mass is added lye from a weighed dropping-bottle until all red powder has disappeared, and merely minute shining green crystals are to be seen at the bottom of the flask. From the number of grammes of potassa lye consumed (1 part KHO and 2 parts H_2O), the quantity of lye is calculated which will be required for neutralising the entire lot.

For converting the ethyl eosic acid into the potassium salt, there are placed in an enamelled and jacketed pan (with a reflux cooler), $2\frac{1}{2}$ parts water and $1\frac{1}{2}$ part alcohol, calculated for the weight of the eosine to be operated upon. The eosine is stirred into the cold alcohol 36 per cent., the pan is closed and heated to boiling. To the boiling mass there is allowed to enter in a thin stream the calculated quantity of potassa-lye, previously heated to 80°, with agitation, which is continued for fifteen minutes after the introduction of the lye. The cold apparatus is opened after the lapse of three days; the mother liquor is drawn from the crystals; the latter are placed on a filter and freed by pressure from the mother liquor; the cakes are once more washed in hot water, filtered, pressed again, and dried on enamelled plates. The yield is 25·3 kilos. of spirit eosine.

In working up the residues, the bromising alcohol is run into an enamelled pan, mixed with half its volume of cold water, which is caused to run in as a thin stream and with agitation. Tetrabromfluoresceine separates out as a red powder. It is allowed to subside, the eosine is washed out perfectly with water, filtered, pressed, and dried. The further process is conducted as in the case of the residues of eosine *A*, by washing with alcohol, and twice recrystallising the sodium salt from alcohol.

The mother liquor separated from the crystals is allowed to stand about eight days, when about 2 kilos. of crystals separate out, which are worked up with the following lot. The mother liquor (now drawn off for the second time) is separated from alcohol in the still. Moderately pure eosic acid may be obtained by precipitating the residues from this apparatus (previously dissolved in water) with hydrochloric acid. It is filtered, washed, and pressed, the cakes are dried, and can then be worked up like the eosine *A* residues.

The working up of the alkaline and acid alcohols by distillation depends upon their reaction. Those of an acid character (the bromising and washing alcohols) are neutralised with milk of lime in a montejus lined with lead, and are then forced into the so-called column apparatus and rectified. The alkaline or neutral alcohols, those from the mother liquors and those which have been merely diluted with water are rectified *per se*, and worked up for alcohol at 96° or 97°. The residue in the still, obtained by working up the acid alcohols, is let off into an autoclave, and when suitably diluted with water forced through a filter-press. The filtrate is worked up for bromine. The contents of the filter-press and the impure coloured liquors obtained in working up the alkaline alcohols go to waste.

Dinitrodibromfluoresceine.—In bromising dinitrofluoresceine in an alcoholic solution (nitro-bromising of fluoresceine in alcohol) there are placed in five enamelled pans 60 kilos. of alcohol at 96° with 7 kilos. of fine fluoresceine, keeping up agitation. To the fluoresceine, which is kept divided by agitation, we add gradually 7 kilos. nitric acid at 72° Tw., and immediately afterwards 7·25 kilos. of bromine, which is drawn directly out of the bottles by means of a syphon. Dibromdinitrofluoresceine, which is sparingly soluble in alcohol, separates out. The pans are allowed to stand undisturbed to the next day. The black liquid is drawn off, and the precipitate is washed once with 30 kilos. of alcohol. The precipitates placed on the filter, after draining, are boiled up in a tub with water, allowed to settle, decanted, and this treatment is repeated until the boiling water begins to be faintly coloured. When this is the case all the acid is washed away. The fine paste is spread out in a thin layer on enamelled dishes on the water-bath and dried. The yield of sifted produce is 63 kilos.:

Fluoresceine.	Alcohol.	Nitric acid.	Bromine.	Washing alcohol.	Dibromdinitro-fluoresceine.
35	300	35	36·25	150	63·0

For nitrising in glacial acetic acid, 30 kilos. of bromeosine are introduced into an enamelled pan on the water-bath, which, according as a more or less fine product is desired, is taken either from a spirit-bromised or a water-bromised sort. To the bromeosine are added 25 kilos. of glacial acetic acid, and the whole is stirred up to a uniform paste, with which 4 kilos. of soda-saltpetre are incorporated by diligent stirring. The pan is then covered and the water-bath is raised to a boil. The reaction begins about 70°–80°, whilst small quantities of nitrous acid and a little glacial acetic acid escape. A uniform temperature is kept up by frequent stirring. After heating for six to eight hours, the red mass has turned to a flesh colour, and the reaction is at an end. The course of the reaction is followed by sampling, and it is brought to an end when a sample dissolved in ammonia and compared with a type-sample produces at once a blue colour upon a slip of filter-paper.

The mass, after cooling, is boiled up in a wooden vat with 500 litres of water. After boiling for about ten minutes it is allowed to settle and the liquor is pressed off. The residue at the bottom is deacidified in the usual manner. The fine flesh-coloured paste is spread in thin layers upon enamelled capsules and dried. Yield, 29½ kilos.

For nitrising in watery solution, 10 kilos. of fluoresceine are dissolved in a double pan in 200 litres of water and 13 kilos. of lye at 62° Tw. In an adjoining double pan there are dissolved 12 kilos. of bromine in a mixture of 20 kilos. of lye at 62° Tw. and 50 kilos. of water. This liquor is used for decomposing sodium hypobromite. When completely cold, the fluoresceine solution and the bromine solution are run into an enamelled pan set in a water-bath, and are further mixed, with constant stirring, with 60 kilos. sulphuric acid at 72° Tw. Yellow bromeosine separates out. 30 kilos. of nitric acid at 72 Tw. are run in, stirring constantly. The admixture of the acids must be effected with refrigeration; but as soon as all the ingredients are together the water-bath is heated to boiling. The heating lasts five to six hours, with occasional stirring. The reddish-yellow eosine is then converted into the flesh-coloured nitrobromeosine. The product, mixed with water in a cask and freed from acid by repeated decantations, is finally filtered and dried on the water-bath in thin layers. The yield is 19½ kilos.:—Fluoresceine, 10; soda, 13; bromine, 12; soda at 62° Tw., 20; sulphuric acid at 72° Tw., 60; nitric acid at 72° Tw., 30.

The dibromdinitrofluoresceine is rendered soluble either by passing over it gaseous ammonia when dried and finely sifted, or as above described, or by adding a solution of potash to the eosine paste stirred up in hot water. The first method yields the ammonium salt, the second that of sodium, and the third that of potassium.

The ammonium salt of nitrobromfluoresceine is produced in the same manner as the ammonium salt of tetrabromfluoresceine, namely, by conducting dry ammonia over the free acid in an ammonia-chest. There are used 30 kilos. eosic acid obtained by either of the two first methods above described. The yield is 31·9 kilos. As very pure products are obtained by bromising in alcohol or glacial acetic acid it is recommended to employ here the ammonia method.

For obtaining the sodium salt, 30 kilos. of eosic acid are diffused in 200 litres of water in an enamelled double pan, and heated to 90°. To this liquid, which is kept uniform by agitation, there is added soda-lye, which is run in from a vessel with a cock The addition of soda is stopped before complete neutralisation. This incomplete saturation is in order to separate the pure eosine from the impure colouring matters formed during nitrising, which would ultimately dissolve in the soda with the formation of salts, but which remain undissolved as long as the soda added is insufficient. The progress of the solution of the free acids is observed by means of a slip of filter-paper,

and soda-lye is added, until a drop of the solution taken out with a glass rod and let fall upon a slip of filter-paper held aslant does not give a pure, uniform spot, but shows a small quantity of a solid powdery residue at the point of contact. On the quantity of this residue depends the purity of the product. The saturation may, however, be carried rather far. The deep-red liquid, containing little sediment, is allowed to settle in a tall cask, drawn off after standing for two days, and evaporated down in a drying-pan. The yield is 29½ kilos. of scarlet.

The potassium salt is obtained with potassium-lye exactly as above described. The potash must be cautiously added to the hot eosine liquid in small portions. The further conduct of the operation and the testing are effected as with the sodium salt. The yield is 30 kilos.

Tetraiodofluoresceine. Erythrosine B.—The iodising of the fluoresceine is effected in the same manner as the bromising, only with the difference that no mineral acid, but acetic acid, is used for setting up the reaction, as it can dissolve iodine, and hence allows it to react in a finer state of division.

In an enamelled double pan of 100 litres capacity there are dissolved 6 kilos. fluoresceine in a hot mixture of 8 kilos. soda-lye at 62° Tw. and 60 litres of water. In a similar pan of equal size there are dissolved 24 kilos. of iodine (not sublimed) in 27 to 28 kilos. of soda-lye at 62° Tw. and 60 litres of water. The liquid, which is at first brown, and afterwards colourless, is boiled, and is then run off into a wooden vat of 600 litres capacity (set in a low place), as is also the solution of fluoresceine. After the mixture has been thoroughly stirred 25 kilos. of glacial acetic acid are run out of a stone-ware vessel, in a stream of about the thickness of a finger, into the alkaline mixture, with vigorous stirring. Fluoresceine and iodine are separated out in a state of the finest division, and substitution takes place. When all the glacial acetic acid has been added the iodine is boiled, neutralised with 17 kilos. of lye, and a mixture of 25 litres water and 25 kilos. hydrochloric acid is added within the lapse of three minutes. The vat is then filled up with water, boiled, and allowed to settle. The hot iodine solution is separated after about an hour from the red precipitate of tetraiodo fluoresceine by decantation into a wooden vat. The deposit is placed upon an alkaline filter, drained, returned to the cask, and boiled up once more there with about 300 litres of water and 10 kilos. hydrochloric acid. This decantation and boiling are repeated once more, but without the hydrochloric acid. The free iodeosic acid is placed on a filter, allowed to drain thoroughly, the brick-red paste is spread out thinly upon enamelled drying capsules placed on the water-bath, and dried. The red powder is then sifted. The yield is 15 kilos.

For obtaining the ammonium salt the sifted iodeosine is placed upon frames and exposed to the action of ammonia in a chest as above described. The excess of ammonia is cut off as soon as a sample appears completely soluble. The yield is 15·3 kilos. *erythrosine B.*

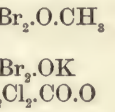
Bi-iodofluoresceine. Erythrosine G.—The less iodised product, consisting chiefly of bi-iodo fluoresceine, is obtained if we use only 16 kilos. iodine instead of 24, proceeding otherwise exactly as above.

Fluoresceine, 6; lye, 8; iodine, 16; lye, 20; acetic acid, 20; lye, 17; hydrochloric acid I., 25 kilos.; hydrochloric acid II., 10; yield, 12·9; sal-ammoniac, 8; CaO, 16; erythrosine G, 13·2.

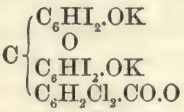
By methylating the eosine the potassium salt of tetrabromfluoresceinemethylether is obtained, and is sold as *erythrine*, spirit-eosine.

Phloxine P is the potassium salt of tetrabromdichlorfluoresceine, which is obtained by the action of bromine upon dichlorfluoresceine. By methylating phloxine we obtain *cyanosine*, and *cyanosine B* is formed by ethylating tetrabromtetrachlorfluoresceine, whilst *phloxine T* is produced by bromising tetrachlorfluoresceine in an alcoholic

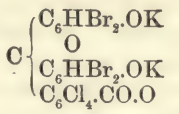
solution. *Rose Bengale* is formed by the action of iodine upon dichlorfluoresceine, and *Rose Bengale B* by iodising tetrachlorfluoresceine, *e.g.* :—



Cyanosine.



Rose Bengale.



Rose Bengale B.

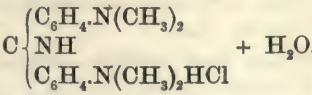
Resorcine Blue, *Lacmoid*, is formed by heating resorcine with sodium nitrite. By the action of nitrous acid upon resorcine there is produced *dinitroresorcine*, or *solid Green*, $C_6H_4(NO_2)_2$ or $C_6H_2(O.NOH)_2$, which dyes a green on tissues mordanted with iron.

With tetramethyldiamidobenzophenon chloride resorcine gives *resorcine violet*, which is not met with in commerce.

Auramines.—The simplest members of this series are pure yellow colouring matters, which are formed from the tetra-alkylised diamidobenzophenones (or their haloid derivatives) by the action of ammonia upon the methan residue. From these dyes there are prepared phenyl-, tolyl-, naphthyl-auramines of redder or browner tones by heating with aniline, its homologues and its derivatives (substituted in the benzol nucleus), naphthylamine, &c., with the elimination of ammonia. These same substituted auramines are obtained by the immediate action of the amines concerned upon the above-named ketone bases and their haloid derivatives. If tetramethyldiamidobenzophenone and tetraethyldiamidobenzophenone are used, practically useful results have been obtained hitherto with ammonia, aniline, para- and orthotoluidine, metaxylidine and phenylenediamine, cumidine, α and β naphthylamine.

Free ammonia does not act upon the ketone bases, but upon their haloid derivatives. If, *e.g.*, the product obtained by treating tetramethyldiamidobenzophenone with phosphorus chloride in presence of an indifferent solvent is mixed with concentrated ammonia, with good refrigeration, a yellow colour at once appears, and after some time auramine separates out in a crystalline form. More advantageous is the direct action of the ketone bases, which, on heating with ammonium chloride, acetate, tartrate, benzoate, or sulphocyanide, especially with the aid of zinc chloride or other dehydrating agents, can be easily converted into auramines.

There is put into an enamelled pan provided with an oil or air bath, and previously heated to about 200°— *e.g.*, an intimate mixture of 25 kilos. tetramethyldiamidobenzophenone (obtained by saturating dimethylaniline with $COCl_2$)—25 kilos. sal-ammoniac, and 25 kilos. zinc chloride. The mixture gradually melts down and takes a deep yellow colour. To promote the fusion of the mass it is thoroughly stirred from time to time. If the temperature within the melt is about 150° to 160°, the colouring matter is formed in from three to five hours. The end of the reaction is recognised when a sample of the melt dissolves almost completely in hot water. The cold, solid mass is broken up, and first treated with cold water acidified slightly by hydrochloric acid, so as to remove the bulk of the excess of sal-ammoniac and zinc chloride. The residue is then exhausted with hot water, and the extract, previously filtered from any unattacked ketone base, is precipitated with sodium chloride. The crystalline precipitate can then be easily rendered perfectly pure by re-crystallisation from water. The colouring matter is the hydrochlorate of imidotetramethyldiamidodiphenylmethan—



The hydrochlorate, sulphate, and acetate are relatively easily soluble in water, less easily the double zinc chlorides, whilst the hydriodic and hydrosulphocyanic salts

dissolve with difficulty, or scarcely in the cold. The watery and alcoholic solutions are not fluorescent. On the addition of mineral acids there is at first no change; but on prolonged standing, or more rapidly when heated, there then occurs decolorisation, whilst the ketone-base is re-formed and ammonia is split off. Alkaline reducing agents—*e.g.*, sodium amalgam—slowly decolorise the alcoholic solution in the cold. On the addition of water there separates out a colourless crystalline reduction product. The acetic solution is scarcely coloured, but on heating it at once takes a deep blue colour. This process depends on splitting up the reduction product into ammonia and tetramethyldiamidobenzhydrol. On heating the auramine with aniline to the boiling-point of the latter, ammonia is evolved, and the mixture contains the orange-yellow dye *phenylauramine.*

Nitrosodimethylaniline, $C_6H_4.NO.N(CH_3)_2$, a very important material for the preparation of many colouring matters, is obtained by dissolving 2 parts dimethylaniline in 5 parts strong hydrochloric acid and 10 parts of water, and adding the required quantity of sodium nitrite. Nitrosodimethylaniline separates out.

This salt yields with metaphenylenediamine the hydrochlorate of dimethyldiamidophenazine, called *neutral violet;* with metatoluylenediamine it forms the hydrochlorate of dimethyldiamidotoluphenazine, *neutral red.*

Both are spoken of as *eurhodines.*

Indophenol,

$$N\begin{cases}C_6H_4.N.(CH_3)_2,\\ C_{10}H_6O\end{cases}$$

is formed by the action of nitrosodimethylaniline upon *a*-naphthol, or by the oxidation of amidomethylaniline and *a*-naphthol. It is insoluble in water.

New Blue, Naphthylenene Blue R, *Cotton Blue R*, *Fast Blue for Cotton*, the chloride of dimethylphenylammonium-β-naphthoxazine,

$$ClN(CH_3)_2C_6H_3\begin{cases}N\\ O\end{cases}C_{10}H_6,$$

is formed from nitrosodimethylaniline-β-naphthol. It is easily soluble in water, with a violet-blue colour.

The similar colouring matter, *Muscarine*, is formed from nitrosodimethylaniline hydrochlorate with *a*-dioxynaphthaline, and with *a*-naphthylamine it yields *Nile Blue.*

Gallocyanine (*Solid Violet*), the chloride of dimethylphenylammoniumdioxypheneoxazine carbonic acid, is formed from nitrosodomethylaniline with gallic acid. It is insoluble in water, whilst the colouring matter, *Prune*, obtained in a similar manner from gallic methyl ether, is easily soluble.

Methylene Blue is the hydrochlorate or zinc double chloride of tetramethylthionine. According to Caro, dimethylaniline is converted by sodium nitrite into nitrosodimethylaniline, reduced by hydrogen sulphide to amidodimethylaniline, which is finally oxidised by ferric chloride. Or it may be first oxidised and then treated with ferric chloride. The colouring matter is precipitated from the splendid blue solution with common salt and zinc chloride. Or nitrosodimethylaniline is dissolved in sulphuric acid, of sp. gr. 1·40, converted by zinc sulphide into the leuko-base of methylene-blue, which is then oxidised (*Ethylene Blue*).

Methylene Blue is characterised by its fine blue tone, slightly verging on green, and its fastness against soap and light. It dissolves readily in water, dyes cotton without a mordant, and is distinguished from aniline blues by the odour of dimethylaniline which it evolves if boiled with caustic alkali.

The manufacture of methylene blue includes, according to Mühlhäusen—1, the production of the solution of nitrosodimethylaniline; 2, the sulphurising; 3, the oxidation; 4, the precipitation; and lastly, the filtration.

For obtaining the solution of nitrosodimethylaniline there is prepared a solution

of dimethylaniline hydrochlorate and a solution of sodium nitrite. Into each of three vats there are poured 1200 litres of water. To this is added a mixture, previously prepared, of 10 kilos. dimethylaniline and 1 carboy of hydrochloric acid at 30° Tw., which are best mixed in an enamelled vessel, stirring the dimethylaniline into the hydrochloric acid, which has been previously diluted with about 50 litres of water.

For preparing the nitrite solution there is put into each nitrite vessel corresponding to the three colour vats 6·6 kilos. of sodium nitrite (at 98 per cent.) and about 150 kilos. of water. After about twelve hours the cocks of the nitrite vessels are opened, and the solution is run during two hours through a leaden funnel-tube, which reaches to the bottom of the colour vats. The temperature of the solution before nitroising is from 8° to 9°, but afterwards from 10° to 12°. In summer or winter the temperature is regulated with ice or steam. Constant agitation is kept up during the nitroising, and afterwards 2 carboys of hydrochloric acid are added to each vat.

The object of the sulphurising is to expel the excess of nitrous acid, to reduce the nitroso-compound to an amine, and to saturate the liquid with hydrogen sulphide. The development of the sulphuretted hydrogen is effected with quite fresh moist soda-mud (*i.e.*, vat-waste). A pail filled with soda-mud has the net weight of 35 kilos. The contents of two such pails suffice to expel the nitrous acid of all the three vats. Into each vat there is put by means of a shovel $\frac{1}{3}$ pailful. A yellowish-green froth appears, and on adding another $\frac{1}{3}$, orange vapours of nitrous acid are expelled by the sulphuretted hydrogen, which dissolves in the water. These operations require constant stirring, and last about five minutes. The liquid then smells of sulphuretted hydrogen.

Previous to reduction we then add to each vat two more carboys of hydrochloric acid, and then begin to introduce the vat-waste. Each vat receives at intervals of $1\frac{1}{2}$ to 2 hours four or five pails of the vat-waste. On adding each pail (which takes about two minutes) the agitator is set in action in order to distribute the mud equally at the bottom of the vats. Caution is here needed, as the mass easily overflows, which may be prevented by stopping the agitator in time. After the mud has been thrown in, the agitator is stopped, so that the development of the sulphuretted hydrogen may proceed quietly and slowly, and it may have full opportunity for dissolving, but little for escaping. The reduction is generally complete by the introduction of the fourth pail. A strip of filter-paper dipped in the liquid should no longer show the characteristic nitrose margin. As the liquid remains standing over night, half or one pail is added for subsequent development, according as the reduction and saturation have made more or less progress.

After adding the soda-mud the solution becomes a milky white, and contains chiefly amidodimethyline hydrochlorate and small quantities of a sulphuretted base, which both yield the blue colouring matter, also milk of sulphur and the residue of the mud, along with some sulphide not attacked, and which may subsequently cause irregularities in the production of the colouring matter. The calcium chloride formed does not come into consideration.

During the sulphurising the liquor undergoes a series of changes in colour, which prove that not merely diamine but colouring matter is formed, which is partly reduced to methylene white, and partly converted into methylene red by being more highly sulphured. The following table shows the observations made during such a reduction :—

Number of Pails.	Heat after adding Mud.	Time.	Reaction on Filter-paper.	Appearance of Liquor.
1*	16°	9.20 a.m.	Pure yellow	Brownish-yellow
		10.15 „	Yellow, orange	Black-green
		10.30 „	Yellow, orange, red	Black
2	17½	11.5 „		Black-brown
		11.25 „	Yellow, red, blue	Black
		11.45 „	Yellow, red, very strong	Deep black
3	19	12.0 noon		Chocolate
		12.30 p.m.	Yellow, blue and red	Blue
4	20	1.50 „		Very blue
5†	21	2.50 „		Red
		4.0 „		Colourless

The oxidation is effected by the addition of ferric chloride, of sp. gr. 1·16 to 1·17, which corresponds to 20–21 per cent. Fe_2Cl_6, to the sulphured liquid. Ferric chloride is added until the smell of sulphuretted hydrogen has entirely disappeared and a slight excess of iron chloride is present. For the oxidation, four carboys of ferric chloride, containing each 70 kilos. of the above-mentioned sp. gr., are nearly always sufficient.

Whether enough has been added can be judged at once by the eye. The oxidised liquor must appear of a deep blue; if it is reddish-blue the oxidation is not quite sufficient.

It sometimes happens that the oxidised liquid, after standing for some time, again evolves sulphuretted hydrogen; in this case also a little more ferric chloride is to be added. These accidents are due either to an irregular introduction of the mud or to imperfect stirring.

The tests for ascertaining whether a vat has received enough ferric chloride are the following :—A sample precipitated with common salt and a little zinc chloride is placed upon a slip of filter-paper, and the opposite margin is touched with a solution of potassium ferrocyanide; if a faint blue spot appears where the two liquids meet, sufficient ferric chloride has been added. If, on the contrary, a slip of filter-paper dipped in the colour-liquor becomes darker if touched with ferric chloride, more ferric chloride must be added to the bulk.

When the solutions are perfectly oxidised, the colouring matter is salted out.

For precipitation 180 kilos. of rock-salt are stirred into each vat, and as this effects only a partial precipitation, there are further added to each 25 kilos. zinc chloride at sp. gr. 1·5.

In order to ascertain whether the colouring matter is completely precipitated, a slip of filter-paper is dipped into the liquid and examined by reflected light; if all the colour has been deposited we see blue flocks on a red ground. If the ground is blue or blueish-red, more salt and zinc chloride must be added. As soon as the test indicates complete precipitation, the liquid is at once filtered through a double woollen filter laid over a tub.

The filtration is effected with constant agitation, and takes two to three hours. The crude colour is on the filter, and the red liquid is caught in the tub below. In the upper colour-vat there is still a residue. It is baled into a wooden trough and elutriated with water until it no longer gives off any colour. The watery extract is placed along with the crude colour in the extraction cask; the residue is thrown away. The crude colour is turned over with a wooden shovel to promote drainage and is then ready for extraction.

The crude colour consists of methylene blue, a residue of mud, sulphur, and dregs of salt tinged with blue.

* Initial temperature, 14°.

† The fifth pail was not entirely added.

The red filtrate is worked up for a zinc colour; 36 kilos. of zinc powder are stirred up to a paste with a little water, to each vat there are allowed, therefore, 12 kilos. of zinc. The paste is put in with iron spoons; a spoonful being briskly stirred into each vat every ten minutes. The liquid foams; streams of sulphuretted hydrogen escape. Zinc is thus added until the liquor becomes colourless. There is now added to each vat, stirring vigorously, a carboy, equal to 70 kilos. ferric chloride, which gives a deep blue solution, from which the colouring matter is at once deposited on account of the salt and zinc chloride present. The contents of the vats, after being well stirred up, are filtered. The liquid flows away and a zinc colour remains on the filter.

In order to work up the crude colour, the dissolving cask is filled up with water and heated with steam to 24°. Into the water, which is mixed with 18 kilos. ferric chloride, is poured the crude colour from six vats; it is stirred up until the water is perfectly saturated with colouring matter and adhering salts, allowed to settle, and the better to clear the liquid a few handfuls of salt are strewn upon the surface of the solution. After twelve hours' rest the coloured liquid is drawn off by means of a syphon into another tub fixed below. On filtering the solution it is well to let the first turbid portions of the filtrate run upon a second filter, also placed over the lower vat, and as soon as the solution is clear it is passed through another filter. The filtrate is now completely salted out with 200 kilos. of clean salt and 30 kilos. zinc chloride. As soon as perfect precipitation has been effected it is filtered at once through a filter below, passing previously through a fine sieve to keep back any coarse particles of rock salt. The colouring matter is then well drained.

The extraction-tub is then again filled with water, heated to 24°, and mixed with 18 kilos. of ferric chloride. The residue left on the filter is stirred in, and the contents are further treated as in extract No. 1. In the third extraction there are only added 9 kilos. ferric chloride, proceeding otherwise as before. As all the salts are dissolved out, this extract yields the finest, strongest, and purest colour. There is, especially in this colour, no more methylene red. Sometimes it may be necessary to make four extracts, but in general three suffice. The residue on the filter and in the cask is placed in the boiling vat, where it is opened up with hydrochloric acid.

The boiling vat is half filled with water; the contents, well stirred up, are mixed with 15 kilos. hydrochloric acid and heated to boiling. The liquid, deep blue at first, becomes pale blue and even colourless, and nitrous acid escapes. As soon as the mass boils, 30 kilos. of ferric chloride are added and filtered at once into a tub below. The purpose of the boiling is the reduction of the methylene blue attached to finely divided sulphur. The filtrate is re-oxidised within the lower cask with 8 kilos. ferric chloride, and then salted out with 150 kilos. rock-salt and 30 kilos. solution of zinc chloride. If the residue in the boiling-vat is not yet entirely opened up (rarely the case), a further extraction is made, the vat being only one-quarter filled with water.

The zinc colour from the six additional casks is placed in the boiling-vat and there stirred up with cold water. The liquid is then allowed to settle for twelve hours and filtered into a tank below. The filtrate is mixed with 10 kilos. ferric chloride, 150 kilos. rock-salt, 30 kilos. solution of zinc chloride, and filtered. The residue on the filter is returned to the vat. The vat is now filled one-quarter with water and heated as above, but only with 40 kilos. salt and 6 kilos. solution zinc chloride. The second extract of zinc colour is generally omitted, working so that when the boiling colour from the raw colour vat arrives in the boiling tank the first extract of the zinc colour is just finished.

According to the working up of the crude colouring matters we have three sorts of extract: pure colour, zinc colour, and boiling colour on the filter. After each filtration the colour on the filter is scraped up and drained in a pointed woollen bag filter; when the last saline liquor runs off. The colours then are mixed in a cask,

and for mixing, water is added until it begins to dissolve colour also, and not merely salts—*i.e.*, until a slip of paper moistened with the solution is coloured faintly blue. The paste, allowed to stand for some hours, is passed through bag filters, wrapped in strong cotton cloths and pressed under a screw-press. The press cakes so obtained are dried on zinc plates, cut up with wooden spatulæ, and dried in a drying-room at 60°.

Instead of mixing the three grades of colour, they may all be worked up separately. The pure colour is then the finest and strongest, and the boiling colour the weakest. If these colours are mixed up with water, the pure colour is blue and the zinc colour and boiling colour grey. Similar is the behaviour of the pressed and dried colours. The yield for every vat is 5 to 6 kilos. The colour when ground is a bronze powder. The following table gives a view of the numbers given above :—

	Oil.	HCl	$NaNO_2$	Na or N Waste.	Fe_2Cl_6	Rock Salt.	$ZnCl_2$	Zinc Powder.	Sodium Chloride.	Yield.
Crude colour . . .	30	1050	19·8	500	1050	540	75	36	—	—
Pure colour A I. . .	—	—	—	—	18	—	30	—	200	—
„ A II. . .	—	—	—	—	18	—	30	—	200	—
„ A III. .	—	—	—	—	9	—	30	—	200	—
Boiling colour A I. .	—	15	—	—	38	—	30	—	150	—
Zinc colour . . .	—	—	—	—	10	—	30	—	150	—
Finished product . .	—	—	—	—	—	—	—	—	—	36
	60	2115	39.6	1000	2193	1080	300	72	900	36

The Zinc Sulphide Process.—If sulphuretted hydrogen is passed into sulphuric acid at 72°–98° Tw., sulphur separates out and the sulphuric acid is reduced to sulphurous acid: $H_2SO_4 + SH_2 = SO_2 + S + 2H_2O$.

The sulphurous acid again is at once decomposed in contact with H_2S with further liberation of sulphur: $SO_2 + 2H_2S = 2H_2O + 3S$.

If this liberation of sulphur takes place in presence of nitrosodimethylaniline sulphate it is converted into a colourless sulphur base, which, when oxidised, yields a blue dye-stuff. For nitrising the following plant is required: 3 enamelled iron pans, each holding 400 litres, fitted with agitators and cooling jackets; 3 sulphuring pans, each containing 1500 litres, with cooling jackets; escapes for sulphuretted hydrogen gas; pressure gauge and cover fitted with a man-hole (the agitator and the pan are lined with lead); a settling beck with a box-filter, and below it an oxidation vat; finally, a purifying system consisting of a redissolving vat and a precipitating tank with a box filter.

The materials needed are: methylaniline, sodium chloride, zinc chloride, of qualities as above mentioned; sulphuric acid, both of 40° and of 130° Tw.; the former is obtained by mixing 23 kilos. sulphuric acid and 50 kilos. water; the latter from 150 kilos. sulphuric acid and 22½ kilos. water. The zinc sulphide must be pure, dry, and finely sifted.

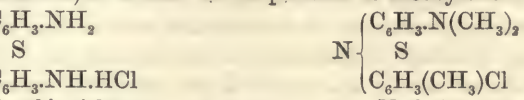
The production of the crude colour comprises: 1, nitrising; 2, sulphuring; 3, clearing; and 4, oxidation.

Into each nitroso-pan there are stirred 10 kilos. methyl-aniline and 75 kilos. of the weak sulphuric acid; the mixture is cooled down to 6° to 8° with ice, and a solution of 6¼ kilos. $NaNO_2$ in 30 kilos. water is run in from a bottle fitted with a cock, and with constant agitation, the temperature not being allowed to rise above 12°. When this operation is at an end the mass is mixed with 175 kilos. of the stronger sulphuric acid, keeping the temperature at 12°. The contents of the pans charged in this manner are now forced up by means of compressed air into the sulphurising pans.

The mass is sulphurised by introducing dry zinc sulphide, ground to an impalpable powder, in lots of 100 kilos., and with continual stirring, keeping the temperature at 20° to 25°. After entering the zinc sulphide the pan is closed, and the contents are digested at 35° to 40°, until the reaction is completed. This is indicated by the decolorising of the solution, which has been in succession light green, blue, dark blue, and finally red. All the contents of the pans are forced into the settling beck, which holds 3000 litres of water, and after being well mixed up they are left to settle for twelve hours. The sulphur is then filtered off, the liquid is boiled again with 5 kilos. of sulphuric acid and 1000 litres water, allowed to subside, and filtered. The united filtrates are oxidised as above described with 5 carboys of ferric chloride, the colouring matter is precipitated with common salt, and filtered.

This colour is purified by redissolving and treating as already described. The blue produced in this manner has a considerably higher tinctorial power than the product obtained by the former process.

Lauth's Violet (*Thionine*) is similar in composition to methylene blue:



Lauth's violet. Methylene blue.

It is obtained by oxidising paraphenylendiamine in an acid solution containing hydrogen sulphide.

Bernthsen heats 10 parts diphenylamine with 4 parts sulphur in a cohobater to 250° to 300° for two hours, or until the end of the reaction is indicated by cessation of the development of sulphuretted hydrogen. The crude thiodiphenylamine is purified by distillation and repeatedly recrystallising from alcohol the light-yellow distillate which solidifies in crystals. For nitrising it is introduced with good cooling and agitation by degrees into 5 parts of nitric acid at 72° Tw. The pasty mixture is then put in much cold water, and the nitro-compound, which separates out as a light-yellow powder, is filtered and washed. It is sparingly soluble in alcohol and benzol, more readily in glacial acetic acid. Instead of free nitric acid the well-known nitrising mixtures can be used. For reducing this nitrised thiodiphenylamine the usual reducing agents may be taken—*e.g.*, stannous chloride, iron, tin, or zinc, with hydrochloric acid, &c. If tin and hydrochloric acid are used, the mixture proceeds very quickly with the application of heat, the nitro-compound dissolves, and there is formed a colourless solution, from which, after tin has been removed by H_2S or zinc, a double zinc chloride is to be obtained by evaporating the hydrochlorate of the leuko-base. This leuko-base is characterised by the reaction that on saturation with ammonia it is on contact with an oxidising agent at once resolved into a violet colouring matter.

The oxidation of the above-mentioned reduction-product can be conveniently effected with the colourless solution freed from tin by means of zinc. On the introduction of ferric chloride in slight excess there appears at once an intense violet precipitation of the sulphuretted colouring matter, which, if necessary, can be completed by the addition of common salt. After filtering off the precipitate it may be further purified by recrystallisation from boiling water. The colour may also be obtained perfectly pure, and in the form of fine crystalline needles, if the concentrated aqueous solution is precipitated by the addition of hydrochloric acid. When dry the colouring matter is a green crystalline powder of a metallic lustre, soluble in concentrated sulphuric acid with a green colour, which, as water is added, becomes first blue and then violet. The colouring base, when set at liberty by alkalies, is red, and dissolves in ether with a yellowish-red colour. If heated in a dry state, the colour is decomposed with liberation of sulphuretted hydrogen. The watery solution has an intense violet colour, and is quickly decolorised by reducing agents, such as zinc-powder, tin,

and hydrochloric acid, solution of hydrosulphite, &c. Oxidising agents quickly restore the colour. The dye-stuff fixes itself directly upon animal fibre, and is peculiarly suitable for dyeing animalised or tanned cottons.

By the introduction of alcohol radicles into the molecule there are formed colouring matters of violet-blue to bluish-green tones.

Induline, *Nigrosine*, *Azodiphenyl Blue*, *Violinaniline*, *Coupier's Blue*, *Fast Blue*, *Printing Blue*, *Acetine Blue* may be best obtained by heating amidoazobenzol with aniline hydrochlorate:

$$\underset{\text{Aniline.}}{C_6H_5.NH_2} + \underset{\text{Amidoazobenzol.}}{C_6H_5.N.NC_6H_4.NH_2} = NH_3 + \underset{\text{Induline.}}{C_{18}H_{15}N_3}$$

Induline is converted into a more valuable colouring matter if it is again treated with aniline salts in presence of aniline. For this purpose we heat in an enamelled cast-iron pan 100 kilos. induline hydrochlorate (azodiphenyl blue), 45 kilos. aniline hydrochlorate, and 200 kilos. of aniline to 160° to 170° for twenty-four hours. The thick melt, when cool, is mixed with 500 litres of alcohol. Fine brass-coloured crystals of the new colouring matter separate out, which are collected on a filter, purified by washing with alcohol, and dried. To effect the formation of induline and its transformation in one and the same operation, we mix in an enamelled pan 100 kilos. diazoamidobenzol with 130 kilos. of aniline hydrochlorate and 300 kilos. pure aniline. The molecular transformation of the diazoamido compound is effected by standing for twenty-four hours, or more rapidly by heating to 40° or 50°, and it is then heated for four to five hours to 110°. The melt is now of a deep violet colour, and still contains traces of amidoazobenzol. It is advantageous, though not strictly necessary, to add 65 more kilos. of aniline hydrochlorate, and then to heat for twenty-four hours to 160° to 170°. The blue thus obtained is then converted into a sulpho-acid by heating with 3 parts sulphuric acid of sp. gr. 1·840 to 110° for six hours. The sulpho-acid is then converted into the sodium salt which forms the commercial product. This new colouring matter, $C_{36}H_{27}N_5HCl$, induline 6B, formed from induline with liberation of ammonia, is distinguished from the well-known colour by its complete insolubility in alcohol and its pure greenish-blue tone, which does not vary in artificial light. The indulines are distinguished by fastness.

Saffranine (*Aniline Rose*) is a mixture of tolusaffranines and phenotolusaffranines. The colouring matter, which dissolves in water with a red colour, is formed by the oxidation of 1 mol. each of aniline, orthotoluidine, and paratoluylendiamine.

Phenosaffranine, $H_2N.C_6H_3.N_2.C_6H_4.C_6H_4.NH_2.Cl$ (*Saffranine B extra*), is formed by oxidising paraphenylendiamine with 2 mols. aniline. It forms green crystals, which dissolve in water with a red colour.

Neutral Blue is formed from nitrosodimethylaniline with phenylnaphthylamine, and *Bâle Blue*, from nitrosodimethylaniline with ditolylnaphthylendiamine.

Giroflé is obtained from nitrosodimethylaniline hydrochlorate and a mixture of meta- and para-xylidine hydrochlorate.

Aurantia (*Imperial Yellow*), the ammonium salt of hexanitrodiphenylamine,

$$N[C_6H_2(NO_2)_3]_2.NH_4,$$

is formed on treating diphenylamine with nitric acid.

2. **Phenol Colouring Matters.**—Phenol serves for the production (besides the azo-dyes) of the following colours:—

Picric Acid (*Trinitrophenol*), $C_6H_2(NO_2)_3OH$, is formed by the action of nitric acid upon phenol, or by treating crystallised sodium phenol sulphonate with nitric acid. It crystallises in yellow leaflets, sparingly soluble in cold water, but readily in alcohol and in hot water. It melts at 122°, and deflagrates if rapidly heated. It is used in dyeing yellows, and in the form of a picrate with aniline green (iodine green), and with indigo or Prussian blue for obtaining green, upon silk or wool.*

* It does not bear soaping.

It has happened that instead of the free acid its sodium salt has been sold under the names of picric acid and aniline yellow, and has given rise to very serious accidents in consequence of its explosive character.

In France large quantities of picric acid are regularly made, not for dyeing, but for producing picrate powder. If treated with potassium cyanide, picric acid yields isopurpuric acid ($C_8H_5N_5O_6$), whilst trinitrocresolic acid yields cresylpurpuric acid ($C_9H_7N_5O_6$), the potassium and ammonium salts of which are known as *garnet brown*. As garnet brown explodes with great violence on slight friction, it is generally sold as a paste. To prevent the paste from drying up it is mixed with a little glycerine.*

Phenyl Brown (*Phenicine, Rotheine*) was obtained by Roth in 1865, and is sometimes used in silk and woollen dyeing. It is formed by treating phenol with a mixture of sulphuric and nitric acids. Phenyl brown is an amorphous powder—a mixture of two colouring matters, the one yellow (according to Bolley dinitrophenol, $C_6H_4(NO_2)_2O$), and a blackish-brown compound allied to the humoids. Phenyl brown is no longer met with in commerce.

Flavaurine (*New Yellow*), the ammonium salt of dinitrophenolparasulpho-acid, $C_6H_2(NO_2)_2.SO_3NH_4$, is obtained by treating mononitrophenolparasulpho-acid with nitric acid.

Victoria Yellow (*Saffron substitute, Victoria Orange, Aniline Orange*) is a mixture of the potassium and ammonium salts of dinitro-, ortho-, and para-cresol,

$$C_6H_2.CH_3(NO_2)_2OK,$$

obtained by treating ortho- and para-cresolsulpho-acid or diazotoluol with nitric acid. It has been recently proved that this dye-stuff is poisonous. Hence it cannot be used for colouring articles of food, &c., as a substitute for saffron.†

Aurine $C\begin{Bmatrix} C_6H_4.OH \\ C_6H_4.OH \\ C_6H_4O \end{Bmatrix}$ is obtained by heating 1 part phenol with 0·5 part sulphuric acid (at sp. gr. 1·84) and 0·6 to 0·7 part oxalic acid, to 120° to 130°. The yield is 60 to 70 per cent. It may also be produced by heating a mixture of 1 mol. phenol, 2 mols. cresol, 3 mols. sulphuric acid and pulverised arsenic acid to 120°. On lixiviating the mass with water, aurine remains as a resinous mass of a metallic green colour, yielding a yellowish-red powder. Commercial aurine, also called rosolic acid, contains, besides aurine, oxidised aurine, methylaurine, pseudorosolic acid, &c. It is soluble in water and insoluble in alcohol.

Coralline (*Peonine, Aurine R*) is obtained by treating aurine with ammonia, and is probably rosaniline rosolate.

Azuline (*Azurine, Rosolic Blue*) impure triphenylpararosaniline hydrochlorate, is obtained by heating rosolic acid with aniline.

Here also belongs the substance first isolated by Reichenbach from beechwood tar under the name of *pittacal*. It is now found to consist of the deep-blue salts of eupittonic acid, $C_{25}H_{26}O_9 = C_{19}H_8(O.CH_3)_6O_3$.

Quinoline, C_9H_7N, a constituent of coal-tar, formerly obtained by distilling cinchonine with sodium hydrate, is now obtained from phenol synthetically. Skraup heats 1·4 kilo. of ortho-, meta-, or para-nitrophenol with 2·1 kilos. of one of the three amidophenoles, 6 kilos. glycerine at sp. gr. 1·26, and 5 kilos. sulphuric acid of sp. gr. 1·845, to 130° to 140°. When the reaction is complete, the volatile impurities are distilled off in a current of steam, the mass is neutralised with soda, the volatile orthoquinoline is distilled off in a current of steam, and the other compounds are precipitated with soda.

According to the statement of the works formerly Meister, Lucius and Bruning,

* Garnet brown is scarcely ever used in dyeing.

† In England saffron is rarely used as a colour for food, except in Cornwall.

the orthonitrobenzylidenacetone obtained from benzylidenacetone by nitrising passes into methylquinoline or quinaldine on treatment with reducing agents:—

$$C_6H_4.NO_2.CH.CO.CH_3 + 3H_2 = C_6H_4.C_3H_2.CH_3.N + 3H_2O.$$

For the reduction of orthonitrobenzylidenacetone, stannous chloride and hydrochloric acid are the most suitable. For 20 parts orthonitrobenzylidenacetone, there are used 75 parts stannous chloride and 75 parts hydrochloric acid (of sp. gr. 1·2) diluted with the same quantity of water. The formation of methylquinoline is effected with a strong liberation of heat. The mass is then mixed with hydrate of lime in excess, and the new base is distilled off in a current of steam. Methylquinoline, which may be used in the preparation of the azo-dyes, boils about 240°, and yields very finely crystalline salts. It is also formed from aniline and aldehyde:—

$$C_6H_7N + 2C_2H_4O = C_{10}H_9N + 2H_2O + H_2.$$

According to Döbner and Miller the reaction of the aldehydes with aniline ensues always on the same principle as with acetaldehyde, 2 mols. aldehyde reacting with 1 mol. aniline so that 2 mols. water and one mol. hydrogen are split off.

Acetaldehyde . .	$2C_2H_4O + C_6H_7N = C_{10}H_9N + 2H_2O + H_2$
Propionaldehyde .	$2C_3H_6O + C_6H_7N = C_{12}H_{13}N + 2H_2O + H_2$
Normal Butylaldehyde	$2C_4H_8O + C_6H_7N = C_{14}H_{17}N + 2H_2O + H_2$
Isovaleraldehyde .	$2C_5H_{10}O + C_6H_7N = C_{16}H_{21}N + 2H_2O + H_2$
Œnanthaldehyde .	$2C_7H_{14}O + C_6H_7N = C_{20}H_{29}N + 2H_2O + H_2$

The most important quinoline colours are—

Quinoline Green, the hydrochlorate of tetramethyldiamidodiphenylquinolyl carbinol obtained from quinoline and tetramethyldiamidobenzophenonchloride is not now an article of commerce.

Quinoline Blue, Cyanine, is obtained from the product of the reaction of amyliodide, quinoline, and methylquinoline.

Quinoline Red is produced if benzotrichloride is heated with quinaldine and isoquinoline in presence of zinc chloride. In preparing quinoline red from benzotrichloride and the quinoline of coal-tar, not more than, at the outside, one molecule of quinoline can thus be converted into colouring matters. According to the experiments of A. W. Hofmann in preparing quinoline red the simultaneous presence of isoquinoline and quinaldine is requisite. If a mixture of 1 mol. isoquinoline and 1 mol. quinaldine is heated in presence of zinc chloride and benzotrichloride the colour is formed at 120°, and the yield is much larger. The analysis of the colouring matter leads to the formula $C_{26}H_{19}N_2Cl$, the exact formula which might be expected on the assumption that in its formation 1 mol. quinoline, 1 mol. quinaldine, and 1 mol. benzotrichloride are condensed, whilst 2 mols. hydrochloric acid are split off, as in the formation of malachite green.

$$\underset{\text{Dimethylaniline.}}{C_8H_{11}N} + \underset{\text{Dimethylaniline.}}{C_8H_{11}N} + \underset{\text{Benzotrichloride.}}{C_7H_5Cl_3} = \underset{\text{Malachite green.}}{C_{23}H_{25}N_2Cl} + 2HCl$$

$$\underset{\text{Chinolin.}}{C_9H_7N} + \underset{\text{Chinaldin.}}{C_{10}H_9N} + C_7H_5Cl_3 = \underset{\text{Chinolinroth.}}{C_{26}H_{19}N_2Cl} + 2HCl$$

Quinoline Yellow, $C\begin{Bmatrix} CH.C_9H_6N \\ C_6H_4.CO.O \end{Bmatrix}$, is formed on heating quinaldine with phthalic anhydride and zinc chloride. In order to render it soluble in water it is converted into a sulpho-acid by treatment with concentrated sulphuric acid, and this again is transformed into the sodium salt.

Perhaps as important as the quinoline colouring matters are the quinoline nostrums such as antipyrine and thalline.*

* Of these substances, antipyrine is the only one which has not since been found to be injurious.

Salicylic Acid, $C_6H_4.OH.CO.OH$, formerly obtained from oil of winter-green and other vegetable matters, is now produced synthetically from phenol.

According to Kolbe's directions, phenol is evaporated to dryness with the quantity of soda-lye needed to form phenol sodium, C_6H_5ONa in an iron retort and heated to 180°. Carbon dioxide is then introduced until no more phenol distils over on slowly heating at from 226° to 250°:

$$2C_6H_5ONa + CO_2 = C_6H_5OH + C_6H_4.ONa,COONa.$$

The sodium salicylate obtained is dissolved in water, acidified with hydrochloric acid, the salicylic acid liberated is separated from the lime and purified.

According to the works, formerly Hofmann and Schotensack, phenol and soda-lye are heated in a double pan provided with an agitator in proportion of 3 to 4 mols. evaporated to dust-dryness, phosgene gas is introduced, beginning at 140°, and the temperature is gradually raised to 200°. As soon as the phenol is distilled off to 90 per cent. of its calculated quantity the operation is stopped, the dusty residue of basic sodium salicylate is dissolved in water, and crude salicylic acid is precipitated by means of carbonic acid, the last portion of phenol having first been driven off by a current of steam after the addition of 1 mol. hydrochloric acid to 1 mol. salicylic acid.

At Schering's works, 50 kilos. diphenyl-carbonate and 54 kilos. phenol-sodium are heated in a pan provided with an agitator at from 160° to 170° for six hours. From the product the salicylic acid is separated in the known manner. The reaction takes place according to the equation—

$$OC_6H_5.CO.OC_6H_5 + 2C_6H_5ONa = C_6H_4.ONa.COO.Na + C_6H_5OC_6H_5 + C_6H_5OH.$$

Schroeder finds that sodium salicylate is formed according to the equation—

$$C_6H_5ONa + Na_2CO_3 + CO = C_6H_4.ONa.CO_2Na + NaCHO_2,$$

if carbon monoxide is passed over a mixture of sodium phenylate and sodium carbonate at 200°.

Among the colours obtained from salicylic acid the most important are—

Salicyl Yellow, the mono-bromsalicylic acid or its sodium salt,

$$C_6H_2.Br.NO_2.OH.COOH, \text{ or } C_6H_2Br.NO_2.ONa.COONa.$$

This compound, like *Salicyl Orange*, $C_6H.Br.(NO_2)_2ONa.COONa$, is no longer in use.

Salicylic acid is much used for the preservation of articles of food, as an addition to beer, wine, &c., it is generally considered objectionable.*

3. **Naphthaline Dye-stuffs.**—Naphthaline, $C_{10}H_8$, forms with chlorine addition and substitution products—*e.g. Naphthaline tetrachloride*, $C_{10}H_8Cl_4$, by heating naphthaline with chlorine gas, which is converted into phthalic acid by means of nitric acid. With naphthaline there are formed only substitution products—*e.g.*, $C_{10}H_7Br$. Nitric acid forms in the first place *a*-nitronaphthaline, $C_{10}H_7NO_2$, which is converted by reducing agents into *a*-naphthylamine, $C_{10}H_7NH_2$, or $C_6H_4\begin{cases}CNH_2.CH\\CH.CH\end{cases}$.

According to Witt, naphthaline used for the production of *a*-naphthylamine must have the following properties: the melting point must be exactly 79°, the boiling point 216° to 217°. A little cylinder cast of the product to be tested, exposed to the free air on a plate of glass, should entirely evaporate in a few days without residue and remain white to the last; 1 gramme of the naphthaline heated in a test-tube with pure concentrated sulphuric acid at from 170° to 200° must not colour the acid red, but at the outside only grey.

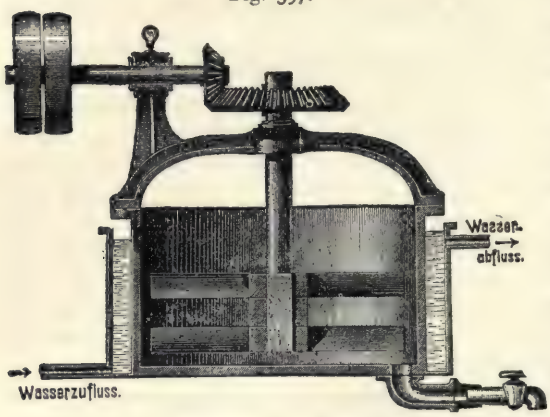
The agitator used in nitrising consists of four to six wings placed obliquely at an angle of 45°. The cast-iron apparatus, provided with a cooling-jacket, is fitted with a lid (left out in Fig. 397), the one half of which may be thrown open, whilst the other has a wide pipe serving for the escape of the gases formed. The lower part of this

* Its use is prohibited in France.

pipe is provided with a steam jacket, so that any naphthaline which congeals in the pipe and causes an obstruction may be melted out from time to time.

The agitator is set in slow action and effects a gentle but complete intermixture of the ingredients. The apparatus is charged with 250 kilos. naphthaline, 200 kilos. nitric acid (72° Tw.), and 200 kilos. sulphuric acid (sp. gr. 1·84), and for dilution 600 kilos. of the spent acid from a former operation. After adding the acid the agitator is put in action, and the introduction of the finely ground naphthaline is commenced. The naphthaline is at once attacked by the acid, the temperature rises, but it is kept from 45° to 50° by regulating the introduction of the material and by letting water flow in the cooling-jacket. At this temperature the nitrising proceeds quietly, and for the quantities given it is completed in a day. The contents are then run out at a cock into a cistern lined with lead. On cooling, the naphthaline is deposited on the surface in the form of a cake, so that the subnatant acid may be kept clear. The cake of nitro-naphthaline is freed from acid by boiling with water in leaded troughs, and finally granulated by an influx of cold water with continual stirring.

Fig. 397.



Explanation of Terms.

Wasserzufluss . . Entrance for water.
Wasserobfluss . . Escape for water.

If nitro-naphthaline is melted or the water-bath is mixed with 10 per cent. of cumol or solvent naphtha, we obtain an oil which remains fluid for a long time, and can be filtered and dried perfectly by means of calcium chloride. The clear mixture is left to itself, when it gradually congeals to a heap of very fine crystals. If the crystalline cake thus obtained is placed under a hydraulic press the solvent which had been added flows off along with a part of the nitro-naphthaline, and may be separated by distillation in a current of steam, and recovered. The press cake consists of fine yellow crystals of nitro-naphthaline, which readily crumble to a light crystalline meal.

The reduction of nitro-naphthaline is effected with iron and hydrochloric acid, exactly as in the preparation of aniline; 600 kilos. of air-dried naphthaline, 800 kilos. of iron borings, and 40 kilos. of hydrochloric acid are used. The iron and the acid are mixed with the addition of some water and heated, and soon after the naphthaline is added in portions through a feeding-socket, which can be closed by a block of wood. The agitator is kept in constant motion. The reaction is rather violent. The addition of the nitro-compound must be so regulated that the entire apparatus is warm to the touch, corresponding to an internal heat of 50°.

When the addition of the nitro-naphthaline is completed the apparatus is kept in action for six to eight hours, the right temperature being maintained by admitting steam through the hollow shaft.

Towards the end of the process samples are drawn from time to time and tested for their proportion of nitro-naphthaline by distillation and dissolving the distillate in hydrochloric acid.

As soon as the reaction is complete, milk of lime is added (50 kilos. are sufficient for the quantities above given), and after thorough stirring the mass is removed

from the apparatus. Witt assumes that the ferrous chloride is the real reducing agent, and that, during the reduction, it is converted into one of the basic chlorides, perhaps Fe_2Cl_4O. In this case the reduction would be expressed by the equation

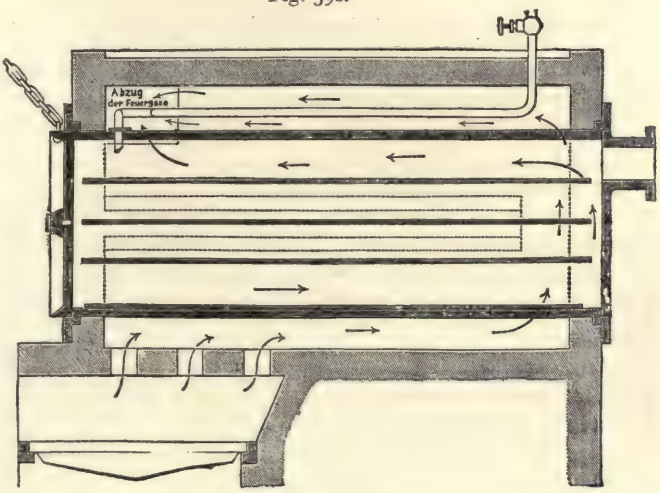
$$24FeCl_2 + 4C_{10}H_7NO_2 + 4H_2O = 12Fe_2Cl_4O + 4C_{10}H_7NH_2.$$

The basic chloride formed is in turn attacked by the excess of iron, or reduced to ferrous chloride, which exerts a new or reducing action upon nitro-naphthaline—

$$12Fe_2Cl_4O + 9Fe = 3Fe_3O_4 + 24FeCl_2.$$

For the distillation of naphthaline there are used the so-called stage-retorts (Figs. 398 and 399), into which the masses to be sublimed are inserted in flat sheet-iron boxes. The retorts are well heated, and in order to convey away quickly the vapours of naphthylamine steam is blown in from above, and the steam-pipe can easily be superheated by the fire gases. The cast-iron cooling-pipes connected with the retorts lie in troughs, in which the condensing water is kept at 60°, so that the pipes may not be blocked up by solidifying naphthylamine. The naphthylamine mixed with some water distils over as a blackish oil, and solidifies in the receivers to a crystalline mass. For conversion into the commercial product it may require to be rectified.

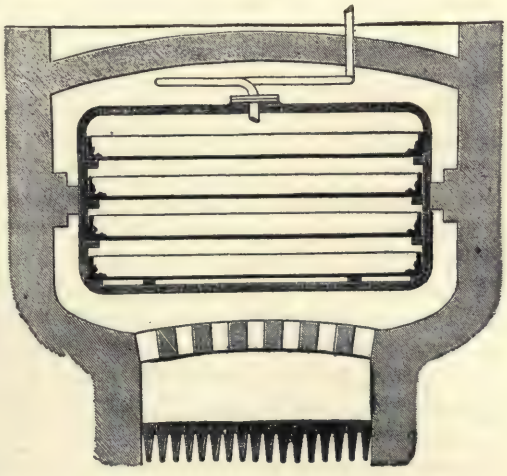
Fig. 398.



Explanation of Terms.

Abzug der Feuergase . . Outlet for combustible gases.

Fig. 399.



β-Naphthylamine,

$$C_6H_4\begin{cases}CH.C.NH_2\\CH.CH\end{cases},$$

is obtained by heating 10 kilos. β-naphthol, 4 kilos. caustic soda, and 4 kilos. sal-ammoniac in an autoclave at from 150° to 160° for 60 to 70 hours, or β-naphthol sodium with sal-ammoniac. It melts at 112° and boils at 294°, whilst *α*-naphthylamine melts at 50° and boils at 300°.

α-Amidoazonaphthaline,

$$N.C_{10}H_6.NH_2,$$

is produced when a solution of 13 parts *α*-naphthylamine is mixed with a solution of 3 parts potassium nitrate and 2 parts caustic potassa. Amidoazonaphthaline separates out.

α-Naphthylamine yields with concentrated sulphuric acid a mixture of two *amidonaphthaline-sulpho-acids*, which are converted by nitrous acid into *diazonaphthaline-*

sulpho-acids, $C_{10}H_6.N_2.SO_3$. With fuming sulphuric acid *a*-naphthylamine yields *a-naphthylamine, a-sulpho-acid*, or *naphthionic acid* $C_6H_4\begin{cases}C.NH_2.CH\\C.SO_3H.CH\end{cases}$.

Naphthaline heated with concentrated sulphuric acid gives a mixture of *a*- and *β*-monosulpho-acid, $C_{10}H_7SO_3H$. The lime salt of *β*-naphthaline sulpho-acid is much less soluble than that of *a*-naphthaline sulpho-acid; hence the acids are generally separated as lime salts.

a-Naphthol, $C_6H_4\begin{cases}C.OH.CH\\CH.CH\end{cases}$, is formed from *a*-naphthylamine and nitrous acid, but is most commonly prepared by melting *a*-naphthaline sulpho-acid with caustic soda.

For the production of *β*-naphthol, $C_6H_4\begin{cases}CH.C.OH\\CH.CH\end{cases}$, 2 parts of caustic soda are melted with a little water and 1 part of *β*-sodium naphthaline sulphate is added, the temperature being slowly raised to 300°. The melt is dissolved in water, decomposed with hydrochloric acid, and the *β*-naphthol, which separates out, is purified by distillation.

If treated with sulphuric acid both the naphthols yield various naphthol-sulpho-acids. Of special importance is the *β*-naphtholmonosulpho-acid (Bayer), Schäffer's *β*-naphtholmonosulpho-acid S, and the two *β*-naphtholdisulpho-acids, R and G.

Phthalic Acid, $C_6H_4.(COOH)_2$, is obtained by heating 1 part naphthalinetetrachloride with 5 to 6 parts of nitric acid. Phthalic anhydride, $C_6H_4(CO)_2O$, is obtained by sublimation.

Naphthaline Red (*Magdala Red, Soudan Red, Naphthaline Scarlet*), the diamido-naphthylnaphthazionium chloride, $C_{30}H_{21}N_4Cl$, is obtained by heating *a*-amidoazonaphthaline with *a-naphthylamine*.

According to Witt, 23·1 kilos. of naphthylendiamine hydrochlorate, 28·6 kilos. of *a*-naphthylamine, and 59·4 kilos. of amidoazonaphthaline are melted together and heated at from 130° to 140°, until the original violet, the colour of the mixture, has changed to a pure red and no longer increases in intensity.*

Martius's Yellow (*Naphthol Yellow, Manchester Yellow*) is ammonium-, sodium-, or calcium-salt of dinitro-*a*-naphthol, $C_6H_4\begin{cases}C.OH.C.NO_2\\C.NO_2.CH.\end{cases}$

It is prepared by treating *a*-napthylamine, *a*-naphtholsulpho-acid, or naphthionic acid with nitric acid.

According to Wickelhaus and Darmstädter, dinitronaphthol is obtained by sulphurising naphthaline; the *β*-acid, which is formed along with the *a*-acid, is removed as a calcium salt, and the former is converted into *a*-naphthol by melting with caustic potassa, $C_{10}H_7SO_2OK + K.OH = C_{10}H_7.OH + K_2SO_3$, and then nitrising the naphthol.

Martius's yellow dyes wool and silk in all tones, from the lightest yellow to a full gold, without a mordant; 1 kilo. of the dry calcium or sodium compound is sufficient to dye 200 kilos. of wool a fine yellow. A chief property of the Martius's yellow is that it bears steaming, whilst picric acid is volatilised along with the watery vapours. It is often used for modifying red and gold-yellow tar colours.

Naphthol Yellow S, Acid Yellow S, the sodium salt of dinitro-*a*-naphtholsulpho acid is obtained by treating *a*-naphtholtrisulpho-acid with nitric acid.

Brilliant Yellow is the sodium salt of dinitro-*a*-naphtholmonosulpho-acid, which is formed by treating *a*-naphtholdisulpho-acid with nitric acid.

Sun Gold, the sodium salt of tetranitro-*a*-naphthol, $C_{10}H_3(NO_2)_4ONa$, no longer occurs in trade.

* It is more permanent than magenta, saffranine, and the eosines, and is characterised by its strong fluorescence.

Naphthol Green B is the ferrous-soda compound of nitroso-β-naphtholmono-sulpho-acid, $C_{10}H_5\left\{\begin{matrix}SO_3Na_2O_3S\\O\qquad\quad O\\NO\ Fe\ ON\end{matrix}\right\}C_{10}H_5$, is obtained by treating the β-naphtholmonosulpho-acid S. with nitrous acid.

Phenanthrene Red, the sodium salt of α-naphthyl-α-sulpho-acid osazonphenanthren-quinone, $C_6H_4.CN.CH.C_{10}H_6.SO_3Na$, is obtained from naphthylhydrazinsulpho-acid and phenanthrenquinone. The azo-colours, capable of being obtained from naphthaline and naphthol, are especially numerous.

4. **Anthracene Colours.*** The most important of the anthracene compounds are the alizarines.

Alizarine, α-β-dioxyanthraquinone, $C_{14}H_8O_4$ or $C_6H_4(CO)_2C_6H_2(OH)_2$. The anthraquinone obtained according to the original process of Graebe and Liebermann was converted by bromising into bibromanthraquinone, $C_{14}H_6BrO_2$, and the latter again was transformed into alizarine potassium (or sodium) by heating with caustic alkali to 180° to 200°. From the alizarine potassium the alizarine was separated by hydrochloric acid.

$$\underset{\text{Bibrom-Anthraquinone.}}{C_{14}H_6Br_2O_2} + 4KOH = \underset{\text{Alizarine potassium.}}{C_{14}H_6K_2O_4} + 2BrK + 2H_2O$$

$$\underset{\text{Alizarine potassium.}}{C_{14}H_6K_2O_4} + 2HCl = \underset{\text{Alizarine.}}{C_{14}H_8O_4} + 2KCl$$

According to the process now generally in use, alizarine is obtained from anthraquinone by treating one part with 4 to 5 parts sulphuric acid of sp. gr. 1·84 at a temperature of from 270° to 290°. It is first converted into anthraquinonedisulpho acid, $C_{14}H_6O_2(HSO_3)_2$; this acid is neutralised with calcium carbonate, the liquid is filtered off from the gypsum, and sodium carbonate is added until all the lime is precipitated. The clear liquid is evaporated to dryness, and the saline mass obtained is converted into alizarine sodium by heating with caustic soda at from 250° to 270°; from the melt thus obtained the alizarine is precipitated with acid.

In converting sublimed anthracene into anthraquinone:

$$C_{14}H_{10} + K_2Cr_2O_7 + 4H_2SO_4 = C_{14}H_8O_2 + K_2Cr_2(SO_4)_4 + 5H_2O:$$

the required quantity of potassium dichromate is first ascertained by a preliminary experiment. The proper quantity of potassium dichromate is placed in a wooden tank lined with lead (fitted with an agitator and holding 3 cubic metres) along with 1500 litres of water which are heated to a boil by admitting steam, the steam is shut off, 100 kilos. powdered anthracene are gradually added, and whilst stirring gently for nine hours the requisite quantity of dilute sulphuric acid (sp. gr. 1·24) is run in. When the reaction is at an end the solution of chrome alum is drawn off in order to convert the chromic oxide (which has been precipitated by lime) into chromate again. The anthraquinone is washed, dried, dissolved in sulphuric acid at 100°, and when cold precipitated by the addition of water.

In preparing the anthraquinone sulpho-acids ordinary sulphuric acid was used at first. But in order to convert the anthraquinone into a sulpho-acid it was necessary to heat to a very high temperature, which involved much loss. At present it is found preferable to use sulphuric acid containing a proportion of sulphuric anhydride. The anthraquinone is mixed with the calculated quantity of sulphuric acid and heated to a higher or lower temperature according as the intention is to produce the mono- or the disulpho-acid. In preparing the disulpho-acid, all the anthraquinone is dissolved, heating until a sample if poured into water dissolves completely, whilst in preparing the mono-acid a portion of the anthraquinone remained undissolved. As far back as 1871 it was known that only the sodium anthraquinone monosulpho-salt yielded

* Compare *Auerbach's Anthracen*, edited by W. Crookes, F.R.S. London: Longmans.

pure alizarine, and the endeavour then was to obtain as pure a monosulphate as possible for obtaining the "blue cast." In the sulphurising process it was not practicable to obtain the monosulpho-acid directly, and the makers were therefore obliged to separate it out from a mixture of the different sulpho-acids. The sulpho-acid obtained at a high temperature was neutralised with lime, and the calcium salt formed was converted into sodium salt by means of sodium carbonate. On evaporating down the solutions of these sodium compounds, white crusts were soon separated out, which, on fusion with alkali, gave a very blue alizarine and proved to be the anthraquinone monosulpho-salt of sodium. This fractional crystallisation required much time, and it was therefore an improvement when it was found that from a mixture of the mono- and the disulpho-acid the former could be precipitated first by alkali. It became necessary merely to partially neutralise the acids with caustic soda in order to obtain a precipitate of the monosulpho-salt. This salt was filtered and the filtrate was worked up for alizarine of a "yellow tone."

In melting the anthraquinone sulpho-salts with caustic soda the alkali takes the place of the sulphuric residue in anthraquinone, and there is formed sodium alizarate. Alizarine is formed only out of anthraquinone sulpho-acid. If the alkali were to act upon this acid in such manner that merely the sulphuric residue would be substituted by NaOH, a compound would be formed containing one atom oxygen less than does alizarine: $C_{14}H_7.SO_3NaO_2 + NaOH = C_{14}H_7NaO.O_2 + NaHSO_3$.

This compound is monoxyanthraquinone. If alkali acts upon this compound again it has an oxidising action; one atom hydrogen is replaced by hydroxyl, hydrogen escapes, and alizarine is formed: $C_{14}H_7(O.Na)O_2 + NaOH = C_{14}H_6(NaO)_2O_2 + H_2$.

In the action of alkali upon disulpho-acids, at first the true sulphuric acid residues are replaced by hydroxyls and there are formed compounds isomeric but not identical with alizarine. On further action of the melting alkali one more atom hydrogen is replaced by hydroxyl, and there are formed colouring matters containing more oxygen than the alizarine—*i.e.*, the purpurines.

Under certain circumstances, however, alizarine is also formed from the disulpho-acid, but only in small quantity. To prevent the reducing action of the hydrogen, substance is added which gives off oxygen and oxidises the nascent hydrogen to water. The most suitable substance is potassium chlorate.

The melting process has undergone important changes and has reached a degree of perfection which leaves little room for improvements. The yield of colouring matter has risen from 30 or 40 to 95 to 98 per cent. of the amount theoretically possible.

The form of the autoclaves can be varied at pleasure, but the plates must be strong enough to bear a pressure of 15 to 20 atmospheres, and the arms of the agitator must pass very close over the edge of the vessel so as to prevent the melt from being deposited. The safety-valve is connected with a covered vessel, so that if it is opened the melt is not scattered about. Whether heat is applied in an oil-bath or an air-bath is indifferent, but the latter has the advantage that the temperature can be better regulated and that there is no risk of fire. In the air-bath the temperature can be kept perfectly constant for days, and the entire melt may be finished in thirty-six to forty-eight hours. The autoclave is charged with concentrated soda-lye, the sodium sulphate and the potassium chlorate are added, the autoclave is closed, the agitator set in motion, and the contents heated to 180° to 210°. In a relatively short time the operation is at an end; the melt is forced through a pipe into a vessel of water by means of the pressure in the autoclave. By boiling the violet solution of the melt in water and decomposing the alkaline solution with an acid, the colouring matters are obtained in the state of yellow or orange flocks, which are passed through filter-presses, freed by means of water from sodium chloride or sulphate, and finally made up into pastes of any required strength by adding the calculated quantity of water.

Alizarine VI., or *alizarine I.*, or the *a*-*β*-dioxyanthraquinone, forms an ochre yellow paste. *Alizarine GI.*; *Alizarine FA.*; Flavopurpurine, oxyanthraflavic acid,

$$C_{14}H_8O_5 \text{ or } OH.C_6H_3\begin{Bmatrix}CO\\CO\end{Bmatrix}C_6H_2\begin{Bmatrix}OH\\OH\end{Bmatrix}$$

which is prepared by melting *a*-anthraquinone disulpho acid soda with caustic soda and potassium chlorate, as well as *Alizarine G.D.*, or *Alizarine R.F.* isopurpurine anthrapurpurine, oxyiscanthraflavic acid,

$$C_{14}H_8O_5 \text{ or } OH.C_6H_3\begin{Bmatrix}CO\\CO\end{Bmatrix}C_6H_2\begin{Bmatrix}OH\\OH\end{Bmatrix}$$

are obtained in the same manner from *β*-anthraqunionesulpho acid sodium form brownish-yellow pastes and dye red shades on cotton mordanted with alumina.

Purpurine, trioxyanthraquinone, obtained by the oxidation of alizarine, is $C_{14}H_8O_5$ or $C_6H_4(CO)_2C_6H(OH)_3$.

Alizarine Orange, Alizarine N, *β*-monontroalizarine:

$$C_{14}H_7NO_6 \text{ or } C_6H\begin{Bmatrix}CO\\\\CO\end{Bmatrix}C_6H\begin{Bmatrix}OH\\OH\\NO_2\end{Bmatrix}$$

was first used by Strobel, who formed it by the action of nitrous vapours upon cotton pieces previously printed with alizarine. Subsequently the Baden Aniline Company have supplied this colour, made according to Caro's patent. It is obtained by exposing alizarine spread out in thin layers to the action of nitrous vapours in closed chambers, or by passing nitrous acid into a solution of alizarine in nitro benzol. It crystallises in orange-red leaflets with a green reflection, and melts at 230°.

Alizarine Carmine (Alizarine WS), the sodium salt of alizarine monosulpho acid, $C_{14}H_7O_4.SO_3Na$, is obtained by treating alizarine with concentrated sulphuric acid.

The aluminium salt dyes woollens without a mordant, as do also some other salts. It is better, however, to mordant the wool and dye up with the sodium salt along with tartar. In this manner different tones of colour can be obtained from the same dye-ware by using various mordants. The scarlets, of course, cannot rival those obtained with cochineal, eosine, &c., in brightness, and are also not cheaper, in spite of the low price of artificial alizarine, but they surpass all others in their resistance to light and air. Flannels dyed with alizarine carmine come up bright after every washing, and are not discoloured by the action of perspiration, as are goods dyed with cochineal. They may also be exposed without injury to their beauty to the sun and the weather, an advantage not shared by the other tar-colours. When resistance to light is essential, as for carpets, curtains, army cloths, &c., this colour deserves especial attention.

Alizarine blue, $C_{17}H_9NO_4$ or

$$C_6H_4\begin{Bmatrix}CO\\CO\end{Bmatrix}C_6\begin{Bmatrix}OH\\OH\\N.CH\\CH.CH\end{Bmatrix}$$

is formed on heating with glycerine and sulphuric acid—

$$C_{14}H_7O_4(NO_2) + C_3H_8O_3 = C_{17}H_9NO_4 + 3H_2O + O_2.$$

Alizarine blue is met with in the form of a thin brownish-violet paste, containing 10 per cent. of colour. The colour is almost insoluble in water; in benzol and alcohol it dissolves with difficulty with a red colour. From its benzol solution alizarine blue is obtained in violet-blue needles of a metallic lustre, fusible at 270°. It forms a red solution with concentrated sulphuric acid. If this solution is heated for some time and then diluted with water, a blueish sediment is deposited having the same properties as a dye-ware as the original alizarine blue. The colour is soluble in a solution of sodium bisulphite. The *alizarine blue S* thus obtained contains to one mol. blue, two mols. sodium bisulphite—$C_{17}H_9NO_4.2NaHSO_3$.

In dilute alkalis the dye-ware dissolves with a blue or a greenish-blue colour. After some time, especially in presence of an excess of alkali, it is re-deposited as an insoluble salt. With calcium, strontium, and barium salts, and with those of iron, it forms greenish-blue lakes; with alumina violet blues; with chromic oxide violets, and with tin red violets. Alizarine blue may be reduced, like indigo, in an alkaline solution. With zinc-powder, hyposulphurous acid, or grape-sugar, there is formed in presence of alkali a yellowish-brown solution, from which the colouring matter on exposure to the air is precipitated with a fine blue colour. Unmordanted tissues, if steeped in an alizarine blue vat and then exposed to the air, are dyed a good blue. The vat itself is red, with a blue scum. After airing, the dyed goods are taken through a cold chloride of lime bath or through a solution of potassium chromate mixed with lime. Alizarine blue has not come into general use since the indulines can also be used in the form of a vat.

5. **Azo dyes** contain the group —N = N—. If they contain this group twice they are named tetrazo dyes. They are mostly yellow to orange, more rarely red. Among the great number of these dye-stuffs the following may be mentioned:—

Aniline Yellow (Spirit yellow), amidoazobenzol $C_{12}H_{12}N_3Cl$ or $C_6H_4\begin{cases}NH_2.HCl\\N.N.C_6H_5\end{cases}$ is formed by heating diamidoazobenzol with aniline hydrochlorate. Steel blue crystals, which dissolve in water with a yellow colour and on treatment with fuming sulphuric acid, yield sodium amidoazobenzoldisulphate, $C_{12}H_9N_3(SO_3Na)_2$.

Acid Yellow or *Fast Yellow*.—Fast yellow R, Acid yellow R, Yellow W, the sodium salt of amidoazotoluoldisulpho acid, $C_{14}H_{13}N_3(SO_3Na)_2$, is obtained by treating amidoazotoluol hydrochlorate with fuming sulphuric acid.

Bismarck Brown (*Phenylen Brown*, *Gold Brown*, *Aniline Brown*, *Leather Brown*, *Cinnamon Brown*, $C_{12}H_{15}N_5Cl_2$ or $C_6H_4\begin{cases}NH_2\\N.N.C_6H_3\end{cases}\begin{cases}NH_2\\NH_2.2HCl\end{cases}$), is obtained when dinitrobenzol is amidised with tin and hydrochloric acid and then treated with solution of sodium nitrite. The diazo compound of aniline, if conjugated with naphthol or naphtholsulphuric acid:—

Soudan I, $C_6H_5.N.N.C_{10}H_6[\beta]OH$

Tropäolin oooo, $C_6H_5.N.N.C_{10}H_5\begin{cases}[a]OH\\[a]SO_3Na\end{cases}$

Cochineal scarlet G, $C_6H_5.N.N.C_{10}H_5\begin{cases}[a]OH\\SO_3Na\end{cases}$

Crocein orange: Ponceau G B, $C_6H_5.N.N.C_{10}H_5\begin{cases}[\beta]OH\\SO_3Na\end{cases}$

Orange G, $C_6H_5.N.N.C_{10}H_4\begin{cases}[\beta]OH\\(SO_3Na)_2\end{cases}$

Ponceau 2 G, $C_6H_5.N.N.C_{10}H_4\begin{cases}[\beta]OH\\(SO_3Na)_2\end{cases}$

Diamidoazobenzol with 2 mols. sodium nitrite can be converted into a tetrazo compound, which may unite with 2 mols. naphthylaminesulpho acid, *a*-naphtholsulpho acid, or *β*-naphtholdisulpho acid R, to form azo dyes, which are valuable, as they dye unmordanted cotton directly in a soap-beck.

For instance, 2·12 kilos. pure diamidoazobenzol are dissolved in 5 kilos. hydrochloric acid of 30° Tw. and 100 litres water, and converted into the tetrazo compound by the addition of a solution of 1·38 kilo. sodium nitrite in 20 litres water. The latter is then run into a solution of 6½ kilos. sodium *a*-naphthylamine sulphate and 1½ kilo. soda in 200 litres of water, stirring constantly. After standing for twelve hours, the product of the reaction is dissolved by boiling in water; the colour is salted out, pressed, and dried. It dyes cotton in an alkaline soap-beck a reddish-violet. If in the above

mentioned instance the sodium *a*-naphthylamine sulphate is substituted by 5 kilos. sodium *a*-naphtholmono sulphate there is formed a sparingly soluble dye-stuff, which works on unmordanted cotton with a violet colour.

Azo dyes form the diazo compounds of diamidodiphenyl ketones, $CO(C_6H_4.NH_2)_2$. According to Wichelhaus, the amidoketon is obtained from the salts of rosaniline and pararosaniline, commonly known as magenta, by simply boiling with hydrochloric acid. If this process is continued for some days in a cohobator, replacing the acid which has evaporated, there are obtained from 100 parts of magenta 30 parts amidoketon, with corresponding quantities of aniline or toluidine. The rest of the magenta is unchanged, and may be again applied in a similar manner.

In order to separate the amidoketone from the mixture the solution is rendered alkaline, the aniline or toluidine is driven out by a current of steam, and the residual bases are dissolved in dilute sulphuric acid, taking care that the solution is perfectly neutral. On evaporation the formation of a crystalline scum shows the condition in which the sulphate of the amidoketone crystallises out, the rosaniline or pararosaniline sulphate remaining in solution.

For the production of dye-stuffs, we may either use the amidoketon itself, forming the tetrazo compound by the action of sodium nitrite upon the chloride of this base (with refrigeration), and bringing this then in contact with phenole bases or their sulpho acids. The combination leads—if we, *e.g.*, use resorcine and afterwards salt out with sodium chloride—to a dye-stuff of the formula—

$$CO(C_6H_4N_2)_2.(C_6H_3.(ONa)_2)_2.$$

It dyes an intense yellow on unmordanted cotton in a neutral watery solution.

By combining the tetrazo compound of the amidoketon with the sodium salt of naphthionic acid, a dye-ware is produced of the formula $CO.(C_6H_4N_2)_2(C_{10}H_5(NH_2)SO_3Na)_2$, which dyes unmordanted cotton red in a watery solution. Phenol and its homologues, dimethylaniline, other phenols, and aromatic bases, as well as the sulpho acids of these compounds, unite to form dye-wares with the above-mentioned tetrazo compound.

Benzopurpurine 4 B $\left\{\begin{matrix} C_6H_3\{^{CH_3}_{N.N.C_{10}H_5\{^{NH_2}_{SO_3Na}} \\ C_6H_3\{^{N.N.C_{10}H_5\{^{SO_3Na}_{NH_2}}_{CH_3} \end{matrix}\right\}$ is formed from orthotolidine and 2 mols. naphthionic acid. According to the Berlin Joint-Stock Aniline Company, the tetrazo compounds of tolidine formed by the alkaline reduction of ortho- or paranitrotolual, or a mixture of both (*i.e.*, the technical nitrotoluol), form, with *a*- and *β*-naphthylamine and their mono- and disulpho acids, fine dye-stuffs, partly soluble in spirit and partly in water, which dye unmordanted cottons in a soap-beck a series of tones, from a deep yellowish-red to a bluish-red, and are distinguished from the corresponding benzidine colours by their superior fastness against light and acids.

Whilst the red dye-ware known by the name Congo, obtained from tetrazodiphenyl with *a*-naphthionic acid, is turned brown or black by the slightest trace of acetic acid, the corresponding product from ditetrazoditolyl is not nearly so sensitive to dilute acids and is much faster towards light.

A still greater difference between the benzidine and the tolidine dye-wares appears in conjunction with *β*-naphthylaminesulpho acids, whether they are obtained by directly sulphurising *β*-naphthylamine or by heating Schäffer's *β*-naphtholsulpho acid with ammonia. In both cases tetrazodiphenyl forms with them colouring matters, which are insoluble even in boiling water, and in this state cannot be fixed upon cotton, being therefore technically worthless. On the other hand, tetrazoditolyl forms in conjunction with these sulpho acids dyes soluble in water, which are very valuable from their

fastness against strong acetic acid, and even against dilute mineral acids, as well as by their brilliance.

For the production of these dye-stuffs, aqueous solutions of the tetraditolyl salts are run into the mono- and disulpho-acids of α- and β-naphthylamine, finely divided in water, and the free mineral acids present are neutralised by salts of the organic acids, *e.g.*, sodium acetate. The spirit-dyes thus formed are converted into water-dyes by treatment with fuming sulphuric acid, and have now a great resemblance to the dyes at once obtained in a form soluble in water. For instance, 150 kilos. of toluidine sulphate (diamidoditolyl) obtained from technical nitrotoluol are finely divided in water, mixed with 50 kilos. of hydrochloric acid at 32° Tw. and 22·2 kilos. sodium nitrite, dissolved in 10 litres of water, are slowly run into the solution, which is cooled with ice. In this manner is formed tetrazoditolyl chloride. This solution is then added to an aqueous solution of 58 kilos. of α- and β-naphthylamine hydrochlorate; the free mineral acid is neutralised with sodium acetate, and the mixture is allowed to stand for 24 hours. The dark brown—or bright red—precipitate is filtered off and dried, previous to its conversion into its sulpho acids. Further, 50 kilos. of the dry dye-ware, soluble in spirit, are gradually added, at 15°, to 150 kilos. of fuming sulphuric acid containing 20 per cent. anhydride, with constant stirring, and the deep blue melt obtained is allowed to stand at common temperatures until the sulphurising is complete. It is then poured into water, and the sulpho acid formed is converted into its soda-salt.

According to another procedure, the tetrazoditolyl chloride is added to 73 kilos. of naphthionic acid, *i.e.*, sparingly soluble α-naphthylaminesulpho acid; the free mineral acid is saturated by the addition of sodium acetate, and the mixture is allowed to stand for several days with frequent stirring. There is formed a reddish-brown slimy precipitate, which is converted into its soda-salt by heating and neutralising with soda. On cooling, the dye-stuff is deposited, almost quantitatively, as an orange-red powder, which dyes unmordanted cottons a deep bluish-red.

A scarlet dye-ware, fast against acids and more beautiful than the colours above-named, is obtained from β-naphthylaminesulpho acid, formed by heating Schäffer's β-naphtholsulpho acid with ammonia. After an excess of soda has been added to the aqueous solution of 80 kilos. of sodium β-naphthylaminesulphate, tetrazoditolylchloride is run into it slowly, stirring the mixture and keeping it cool with ice. There is formed a brownish-red precipitate, which redissolves completely after standing for twelve hours. If brine is added to this solution, a red slimy precipitate is obtained, which becomes crystalline on heating, and is the sodium salt of the above-named dye-ware.

Sodium paranitrotolulsulphate in a watery solution, if heated with soda-lye, becomes, according to Leonhardt, a condensation product, soluble in water. It can be used as a yellow on woollens, and by reduction it is converted into an amidosulpho acid; 50 kilos. of sodium paranitrotoluolsulpho salt are dissolved in 700 litres of water and digested with 30 kilos. of soda-lye at 72° Tw. The colour of the liquid passes to an intense yellowish, red. The condensation product formed can be precipitated by the addition of brine.

Either the boiling liquid is mixed with zinc powder until it is colourless, filtered whilst hot, and the new acid is precipitated with hydrochloric acid, or it is strongly acidified and reduced with tin or stannous chloride until a specimen of the liquid, after being rendered alkaline, shows but a faint colour. In either case the acid liberated is purified by dissolving in soda and precipitation with acid, and forms then a yellowish-white powder, quite insoluble in water. The barium salt may be obtained in shining nacreous leaflets by precipitating the concentrated aqueous solution with common salt.

The new amidosulpho acid is characterised by the fact that its sparingly soluble

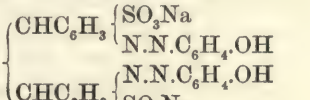
diazo-derivative, in combination with aromatic amines and phenoles or their sulpho salts, forms with the carbon acids yellow, red, brown, and blue dye-stuffs, which give fast colours on vegetable fibres without a mordant. Red and brown-red colours are thus obtained with resorcine, resorcylic acid, orcine, methylaniline, dimethylaniline, diphenylamine, phenylendiamine, β-naphthylamine, and its sulpho acids, α-naphthylaminesulpho acid.

20 kilos. of the sodium salt of the new acid are dissolved in soda and diazotised with 7 kilos. nitrite and 25 kilos. hydrochloric acid. The liquid thus obtained is added to a solution of 15 kilos. β-naphthylamine in 12 kilos. hydrochloric acid and 500 litres water. The free colouring acid separates out; it is filtered, washed, and converted into its sodium salt.

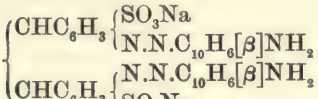
Or we diazotise 20 kilos. of the sodium salt of the amidosulpho acid into the above manner, and pour the solution of the diazo compound to a solution of 28 kilos. of the sodium salt of the β-naphthylaminesulpho acid (obtained from β-naphthol-β-sulpho acid), to which the necessary quantity of sodium acetate has been added to saturate the free mineral acid. The free colouring acid is salted out, washed, and converted into its sodium salt.

Or we diazotise 20 kilos. of the acid as above, and pour the solution into a solution of 19 kilos. diphenylamine in 30 litres of spirit. After standing for a time, the free colouring acid separates out in an insoluble state. It is filtered, washed, and converted into its soluble sodium salt.

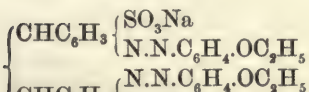
The following dyes are obtained with 1 mol. diamidostilbenedisulpho acid :—With 2 mols. phenol, *brilliant yellow;* with 2 mols. β-naphthylamine, *Hessian purple N;* with 2 mols. naphthionic acid, *Hessian purple P;* with 2 mols. β-naphthylaminemonosulpho acid, *Hessian purple D;* with 2 mols. salicylic acid, *Hessian yellow;* with 1 mol. α-naphthylamine and 1 mol. β-naphthol, *Hessian violet.* By ethylating brilliant yellow there is formed *Chrysophanine:*



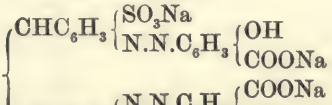
Brilliant yellow.



Hessian purple N.

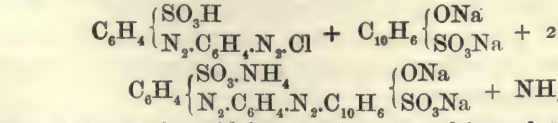


Chrysophenine.



Hessian yellow.

For the production of *Croceine scarlet* 50 kilos. of amidoazobenzolmonosulpho acid are diazotised with hydrochloric acid and sodium nitrite. The diazobenzolsulphuric acid is introduced into a solution of 75 kilos. β-naphthol-α-sulpho acid in 500 litres water and 140 kilos. of 10 per cent. ammonia:



If instead of the sulpho acid free amidoazobenzol is used, the colouring matter has a yellower tone. The homologues of amidoazobenzol yield bluish red dyes, diazobenzol and its homologues reddish yellow ones, α-diazonaphthaline a blue-red dye and β-diazonaphthaline a brick-red colouring matter.

Biebrich scarlet is formed by the action of diazoazobenzol upon β-naphthol; the commercial product consists of the sodium salts of the mono- and di-sulpho acid.

From *a*-naphthylamine and naphthol or the naphtholsulpho acids there are obtained :—

Soudan brown, $C_{10}H_7[a]N.N.C_{10}H_6[a]OH$

Buffalo rubine, $C_{10}H_7[a]N.N.C_{10}H_4\begin{cases}[a]OH\\(SO_3Na)_2\end{cases}$

New coccine R, $C_{10}H_7[a]N.N.C_{10}H^4\begin{cases}[\beta]OH\\(SO_3)_2Ca\end{cases}$

Fast red B, Bordeaux B, $C_{10}H_7[a]N.N.C_{10}H_4\begin{cases}[\beta]OH\\(SO_3Na)_2\end{cases}$

Carmine naphtha, $C_{10}H_7[\beta]N.N.C_{10}H_6[\beta]OH$

Orange I., tropæoline ooo Nt. 1, $C_6H_4\begin{cases}SO_3Na\\N.N.C_{10}H_6[a]OH\end{cases}$ is obtained from sulphanilic and acid *a*-naphthol, the similarly composed Orange II., *tropæoline* ooo No. 2, *chrysaurine*, *gold orange* from sulphanilic acid and β-naphthol. *Orange III.*, *methyl orange*, *tropæoline D*, helianthine, $C_6H_4\begin{cases}SO_3Na\\N.N.C_6H_4N(CH_3)_2\end{cases}$, is obtained from sulphanilic acid and dimethylaniline.

Double brilliant scarlet G is obtained from the diazo compound of β-naphthylamine-monosulpho acid and β-naphthol; it dyes wool a yellowish red in an acid flot. If instead of β-naphthol there is used *a*-naphtholmonosulpho acid we obtain *double scarlet S.*, $C_{10}H_6\begin{cases}SO_3Na\\[\beta]N.N.C_{10}H_5\end{cases}\begin{cases}[a]OH\\[a]SO_3Na_2\end{cases}$, which dyes wool a scarlet in an acid beck.

Woollen black, $C_6H_4\begin{cases}SO_3Na\\N.N.C_6H_3\end{cases}\begin{cases}SO_3Na\\N.N.C_{10}H_6.NH_4\end{cases}\begin{matrix}CH_3\\\end{matrix}\Big\}C_6H_4$, a blue-black azo-dye is obtained by combining paratolyl-β-naphthylamine with the diazo compound of azobenozoldisulpho acid. The paratolyl-β-naphthylamine is dissolved in 20 parts of alcohol and mixed with an equivalent quantity of hydrochloric acid at 31° Tw. An equivalent amount of diazoazobenzoldisulpho acid is introduced, when the free acid of the dyestuff is formed. The latter is salted out with sodium chloride, filtered, and washed until the washings run off colourless. The residue is then taken up in soda-lye, the solution is filtered, and the colouring matter is salted out, when it separates in fine crystalline leaflets. It is filtered, pressed, and dried. In an acid beck it dyes woollens a blue-black.

Congo, $\left[C_6H_4.N.N.C_{10}H_5\begin{cases}NH_2\\SO_3Na\end{cases}\right]_2$, is one of the numerous benzidineazo dyes. It is prepared from benzidine and naphthionic acid, and is by no means permanent.

Congo G R, $\begin{cases}C_6H_4.N.N.C_6H_3\begin{cases}NH_2\\SO_3Na\end{cases}\\C_6H_4.N.N.\beta C_{10}H_5\begin{cases}[a]SO_3Na\\[a]NH_2\end{cases}\end{cases}$, is a red colouring matter obtained from benzidine, amidobenzolsulpho acid, and naphthionsulphuric acid.

For the preparation of mixed azo-dyes, which take upon unmordanted vegetable fibre at once in a soap beck, the German patent 40,954 gives thirty prescriptions, of which the following are specimens :—

1. In order to convert benzidine into the chloride of the tetrazo compound 18·4 kilos. of benzidine are dissolved in 600 litres water which contain 55 kilos. hydrochloric acid at 32° and diazotised with 14 kilos. of sodium nitrite. The solution of the tetrazo compound, made up to 1000 litres, is run, with thorough agitation, into a solution of 20 kilos. of sodium meta-amidobenzol sulphate and 40 kilos. sodium acetate made up

to 500 litres. After acting for one hour the formation of the intermediate product (an orange-yellow insoluble precipitate) is completed. It is then introduced into a solution of 35 kilos. sodium *a*-naphthylamine sulphate and 20 kilos. soda in 500 litres water. After thorough stirring it is let stand for some time, boiled up, filtered, and salted out, yielding a product which dyes cotton a yellowish red in a soap beck.

2. If the intermediate product obtained as according to 1 (from tetrazodiphenyl and meta-amidobenzolsulphuric acid) is mixed, instead of with the quantity of naphthionic salt above given, with a solution of 26 kilos. of sodium *a*-naphthol monosulphate, a colouring matter is obtained which dyes cotton a reddish violet.

3. If, instead of the naphthionic salt in 1, there are used 37 kilos. sodium *β*-naphthol disulphate (R salt), there is obtained a product which dyes cotton a violet-red in an alkaline soap beck.

4. The combination of tetrazodiphenyl with para-amidobenzolsulphuric acid is effected similarly to that with the isomeric meta-amidobenzolsulpho acid. In the preparation of the intermediate product from the *β*-acid there is used the same quantity of benzidine, hydrochloric acid, and sodium nitrite for producing tetrazophenyl, and the latter is made to act upon a solution of 30 kilos. sodium para-amidobenzol sulphate (sulphanilate). The intermediate product is redder than that from the isomeric meta-amidobenzolsulpho acid. For obtaining the dye the intermediate product is made to act upon a solution of 35 kilos. sodium *β*-naphthylamine sulphate in 20 kilos. soda and 500 litres water. The product dyes a brownish orange.

5. If the intermediate product obtained with the proportionate quantities given in 4 is allowed to react on a solution of 14 kilos. phenol in 14 grammes soda-lye at 72° Tw. and 20 kilos. of sodium carbonate, there is formed a yellow dye.

6. A yellow dye is also obtained if the phenol given in 5 is replaced by 15 kilos. salicylic acid.

Other Organic Colouring Matters.—Gallic acid is used for obtaining various colouring matters, such as gallocyanine, galleine, ceruleine, and galloflavine.

Galleine, $C_{20}H_{10}C_7$ or $C\begin{cases} C_6H_2.OH.O \\ O \\ C_6H_2.OH.O \\ C_6H_4.CO.O \end{cases}$, is formed by the action of phthalic anhydride upon pyrogallol in the same manner as phthalic anhydride combines with resorcine to form fluoresceine.

For its preparation Baeyer heats one part phthalic anhydride with two parts of pyrogallol to 190° to 200° for some hours, until the melt becomes thick. The cold melt is dissolved in alcohol, precipitated with water, and the separated galleine is purified by repeated solution and precipitation. In practice he does not set out with pyrogallol, but heats a mixture of gallic acid and phthalic anhydride to 190° to 200°. At this temperature gallic acid is resolved into pyrogallol and carbonic acid; the latter escapes and the former combines with phthalic anhydride to form galleine. The colouring matter is also known as alizarine violet or anthracene violet.

Ceruleine, $C_{20}H_8O_6$, is obtained by dissolving galleine in concentrated sulphuric acid and heating to 190° to 200°. Galleine loses 1 molecule water and yields the dye in question, which is also known as *alizarine green* and *anthracene green*.

Ceruleine is closely connected with phenylanthracene, and passes into this hydrocarbon if distilled over zinc powder. Ceruleine forms when dry a bluish-black shining mass. It dissolves with difficulty in the ordinary solvents with a dirty green colour, but with a fine green colour in the alkalies. With the alkaline disulphites ceruleine forms double compounds soluble in water.

Of these two colours ceruleine is by far the more important. The brownish-red shades of galleine can be obtained quite as easily, though finer and faster, with alizarine, but the rich olive tones of ceruleine have become quite indispensable to the tissue-printer from their fastness against light and soap, as well as by the ease and certainty of their application. Both galleine and ceruleine, like gallocyanine, are most readily fixed by means of the salts of chrome. The soluble bisulphite compound of ceruleine is less frequently used than the paste, to which bisulphite is added, thus producing the soluble double compound in the printing colour itself.

Galloflavine, $C_{13}H_6O_9$, is formed by the oxidation of gallic acid in an alkaline solution by means of atmospheric air.

The Baden Aniline Company dissolve 5 parts gallic acid in 80 parts alcohol at 96° Tralles and 100 parts of water. The solution after cooling down to 5° to 10° is slowly mixed with 17 parts of potassa-lye at 49° Tw., stirring thoroughly, and is exposed to the action of the atmosphere at a temperature not exceeding 10°. For this purpose either a strong current of air is passed through the alkaline solution, or it is exposed to the air in thin layers, a constant renewal of the surface being effected by means of suitable apparatus. The progress of the oxidation is recognised by the increasing olive or greenish-brown colour and by the deposition of a crystalline precipitate, the potassium salt of the new tinctorial acid. To watch the operation there is taken a sample from time to time; it is filtered and the filtrate is shaken with air, observing if after a time there appears a precipitate of the potassium salt insoluble in dilute hydrochloric acid. If no further separation of crystals takes place the process is interrupted to prevent a further oxidation and destruction of the colouring matter which has been formed. The crystalline paste is quickly filtered, pressed, and dissolved in warm water. The solution is slightly supersaturated at about 50° with hydrochloric or sulphuric acid and boiled until the colouring matter separates out in a heap of shining light yellowish-green crystals, which are separated from the reddish-brown solution by filtration. After washing with water at a hand-heat the product is ready for dyeing or printing.

Styrogallol.—Cinnamic and gallic acids unite in presence of a dehydrating agent according to the equation:

$$C_6H_5.CH:CH.COOH + C_6H_2(OH)_3COOH = C_{16}H_{10}O_5 + 2H_2O.$$

Under the same conditions tannin (digallic acid) forms the same condensation product.

10 parts (1 molecule) cinnamic acid and 17 parts of gallic acid are heated for two or three hours to 55° with 150 parts of concentrated sulphuric acid. The melt is poured into an excess of cold water, when styrogallol separates as a pale green powder, consisting of microscopical needles. Like nitroalizarine, it gives with mordants tones ranging from yellow to blackish. The colours bear soaping. Styrogallol can be converted into a soluble sulpho acid by treatment with fuming sulphuric acid. In this state it dyes wool a light yellow.

Tartrazine.—The sodium salt of disulphodiphenylhydrazindioxytartaric acid is obtained by the action of phenylhydrazinmonosulpho acid from diazoamidobenzol upon dioxitartaric acid.

Ten parts of sodium dioxytartrate are diffused in 30 parts of water and mixed with 35 parts hydrochloric acid at 30° Tw. To the clear solution thus obtained there is added a solution of 12·8 parts phenylhydrazin hydrochlorate in 100 parts of water and gently heated. A yellow voluminous precipitate is formed, and after standing twelve hours it is collected on a filter and dried. The light yellow colouring matter when cold is filtered, pressed, and dried; it is readily soluble in water, insoluble in alcohol, and gives a pure yellow, fast to light on animal fibres.

In a corresponding manner *isatine* yellow is obtained by the action of phenylhydrazinparasulpho acid.

Canarine (*persulphocyanogen*), $C_6N_4O_2H_4S_5$, is formed from potassium sulphocyanide by oxidation.

Three kilos. of sulphocyanide are dissolved in 6 litres of hot water in an earthen vessel; 300 grammes potassium chlorate are added and 2·4 kilos. hydrochloric acid are stirred in. The mixture is gently heated, if necessary, until the reaction which sets in after a few minutes has almost entirely subsided. The vessel is then set in cold water, and 1·2 kilo. potassium chlorate and 3·6 kilos. hydrochloric acid are gradually added in small lots. The temperature of the mixture must be kept at about 80°. The orange-coloured precipitate formed is washed by decantation three times with hot water, collected on a linen strainer, washed until neutral, and dried.

For purification this crude product is heated to solution with an equal weight of potassium hydrate and 20 parts of distilled water until dissolved. The dark-red solution is filtered through wool, and when it is cooled down to 40° it is mixed with 20 parts ethyl alcohol at 90 per cent., and the whole is set aside for twenty-four hours. The reddish-orange, granular crystalline precipitate of the potash compound of the colouring matter is filtered, pressed, and dried; the filtrate, after the alcohol has been distilled off, is melted down for potassium ferrocyanide. In order to separate the colouring matter from the potassium compound it is dissolved in 10 parts of water and the solution is mixed with hydrochloric acid enough to precipitate the colouring matter; the brown precipitate formed is washed, filtered, and dried.

The aqueous solutions of canarine-alkaline salts dye cotton, without mordants, shades of maize, yellow, and orange. The colours bear soaping and light. For making up the dye beck, one part canarine, one part potassium hydrate, and 400 parts water are heated to boiling, and one part curd soap is added, or two parts canarine potassium are dissolved in 400 parts water and the part of soap is added.

Goppelsroeder obtains persulphocyanogen by the electrolysis of an aqueous solution of potassium sulphocyanide as an orange-yellow deposit at the positive pole. He has also formed and fixed canarine simultaneously by electrolysis upon vegetable and animal fibres.

Murexide, $C_8H_4(NH_4)N_5O_6$, has been already mentioned.

Lampblack (*soot*) is obtained by the imperfect combustion of resin, gas-tar, oils, &c. The furnaces consist of one or two slightly ascending combustion shafts, *A* (Fig. 400 and 401), in which the solids to be burnt are thrown in in front, whilst tar and oils are

Fig. 400.

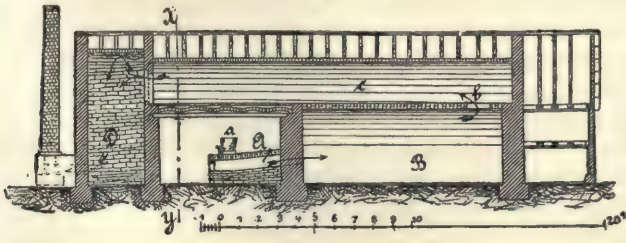


Fig. 401.



Explanation of Term.

Schnitt x-y . . Section x-y.

passed in through iron pipes from the vessels, *a*. The smoke fumes pass from there into the first massive cooling chamber, *B*, through *b* into the long chamber, *C*, extending above it, then into the tower, *D*, divided by a partition into two perpendicular

compartments, and finally through a regulating chimney into the air outside. A coarse cloth, stretched across the half of the tower, serves to keep back the last residues of soot.

The materials are ignited every Tuesday morning, and the combustion is kept up until Saturday evening, with cessations only from 9 or 10 P.M. to 4 or 5 A.M. On Sunday the furnaces cool, and on Monday they are emptied. From 100 parts of tar the yield of lampblack is 25 parts, and from 100 parts of dregs of resin 20 parts.

Finer blacks are obtained by burning mineral oils in lamps; the flame strikes upon cold surfaces, on which the liberated carbon is deposited as lampblack.

Lampblack is used in the production of printing-inks, Indian inks, and as an admixture to some painters' colours.*

EXAMINATION OF COLOURING MATTERS.†

The first point to be ascertained is whether a sample—be it a dry powder, a paste, or a liquid—is a unitary, homogeneous substance or a mixture. To this end, Slater‡ places a drop of the solution upon a piece of filter-paper.

If the colour is homogeneous, the spot produced will be alike throughout. If the colour is a mixture there are seen rings of different colours.

Goppelsroeder§ about the same time applied the same principle in a manner which is often more convenient. He suspends slips of filter-paper so as to dip into the solution of the dye-stuff. If we have to do with a mixture, the different colours will ascend to different heights on the slip, forming a succession of bands.

If time is not a pressing object, a portion of the colour may be dissolved, and swatches of woollen and silken tissues may be dyed successively until the bath is exhausted, noting the order of the swatches. If the colour is homogeneous, the first and the last swatch will display exactly the same tone, but, if it is a mixture, a difference will be observed, some one of the ingredients combining more readily with the fibre than the others.

In the case of the azo dyes, we may utilise their property of dissolving in sulphuric acid with different colours. Pure, clean, concentrated sulphuric acid is placed in a white porcelain capsule; a few fine granules of the dye are sprinkled upon the acid, and the tones of colour which they produce are observed. Mixtures may thus often be detected, especially as the reaction is very sensitive.

Besides the joint presence of different colours, mineral impurities are often found, such as potassium and sodium carbonates, common salt, sodium and magnesium sulphates, and dextrine. These substances are not always due to intentional fraud, but are residues of matters used in the process of manufacture and not fully removed. Common salt is found in almost every soluble colouring matter which is not capable of crystallisation. A small part of the dye is ignited and chlorine is tested for. Sodium sulphate is chiefly found in the azo dyes. The dye is dissolved in water, salted out with chemically pure sodium chloride, and sulphuric acid is sought for in the filtrate in the ordinary manner. Magnesium sulphate is rarely used in place of Glauber's salt. Alkaline carbonates may be used in case of the phthaleines. Dextrine is recognised by the smell which it gives off on dissolving the dye in water, and which resembles that of bugs. Or the colouring matter may be extracted with concentrated alcohol, which leaves dextrine undissolved.

* On the coal-tar colours the reader may compare *The Chemistry of the Coal-tar Colours*, by Benedikt and Knecht. London: G. Bell & Sons.

† Section added by the Editor.

‡ *Manual of Colours and Dye-wares.*

§ *Capillar Analyse und ihre Anwendungen*: Mulhouse, Wenz & Peters.

In carrying out the systematic examination of colouring matters, we mix a moderately concentrated solution of the dye with solution of tannin (25 parts tannin, 25 sodium acetate, and 250 water). An excess of tannin is to be avoided (since the precipitate is often soluble in excess), and the liquid is then heated, as certain sulphonised derivatives of triphenylmethane form precipitates which redissolve at higher temperatures. In the presence of a basic colouring matter the filtrate should be nearly colourless after the addition of the solution of tannin.

We reduce the basic dye-wares with zinc-powder and hydrochloric acid; after filtration, we saturate with sodium acetate, since an excess of hydrochloric acid may form acid salts from the basic colours after re-oxidation, having different colours from those of the neutral salts. In reducing Bismarck brown and chrysoidine, there are formed di- and tri-amines, which are easily oxidised in contact with the air, and take a brownish-red colour. It is therefore necessary, especially in the case of the brown and the yellow basic colours, to compare the colour of the reduced and the re-oxidised dye-stuff with that of the original solution. After the reduced solution has been dropped upon filter-paper, it is advantageous to assist the oxidation by heating it slightly over a flame. Certain dye-stuffs become oxidised with such rapidity that the original colour reappears during filtration.

Acid Colouring Matters.—The reduction of the non-fluorescent yellow, orange, ponceau, and claret dye-wares must be effected with great caution. It is best to reduce with zinc powder and hydrochloric acid and neutralise with sodium acetate, since the nitro groups which may be present in the sample would not be reduced quickly enough if ammonia or acetic acid were used. It is prudent to compare the reduced and re-oxidised solution with the original solution of the colouring matter, since in the reduction of the nitro or azo colours there are formed diamines or amido phenoles, which on oxidation produce dirty-yellow or brown tones. To this section (azo dye-wares) belongs likewise erythrosine, for in its reduction iodine is liberated with re-formation of fluoresceine. All colours not mentioned may be reduced with zinc powder and acetic acid or ammonia. In the reduction of the acid dyes the solution, as soon as the zinc powder has been added to it, should be rendered colourless, or should at most have merely a faint yellowish or reddish tint. The nitrofluoresceine derivatives and the azo dyes may be easily recognised if they are burnt. There are formed upon the sheet platinum "Pharaoh's serpents," especially on working with a large quantity—say 0·5 gramme. In order to detect the nitro groups in the light-yellow colouring matters it is necessary, before ignition, to mix them (*e.g.*, picric acid) with a little soda.

It is very difficult to reduce "alizarine S" completely; it is placed in the last column of Table B., under the heading "The colour of the ammoniacal solution reappears." But if the reduction is carried too far the original colour does not reappear.

All the sulphonised amido-azo and tetrazo colouring matters are almost decolorised if they are reduced with zinc-powder and ammonia, without heat. After filtration the solution is a pale yellow, and if it is poured upon filter-paper and heated it causes yellow spots. The azo colours produce no spots, or, at most, show a dirty brown. The reactions with barium or calcium chloride must be tried with a concentrated solution of the colouring matters. As sodium sulphate is contained in most azo colours, turbidity cannot be reckoned as a reaction. The sulphuric acid test must be carried out as directed above.

Artificial Colours Soluble in Water.

The aqueous solution is mixed with solution of tannin.

A. *There is formed a Precipitate.*

Basic Colouring Matters.

The aqueous solution is reduced with zinc-powder and hydrochloric acid, neutralised, and placed upon filter-paper.

The original colour returns.					Original colour does not return.
Red.	Yellow and Orange.	Green.	Blue.	Violet.	
Magenta	Phosphine	Malachite green	Methylene blue	Methyl violet	Chrysoidine
Toluylen red (Cassella)	Flavaniline	Brilliant green	New blue (Cassella)	Hofmann's violet	Bismarck brown
Safranine		Methyl green	Muscarine (Durand and Huguenin)	Mauveine	Auramine
				Amethyst blue	Victoria blue
				Crystal violet	

B. *No Precipitate is formed.*

Acid Colours.

The aqueous solution is reduced with zinc-powder and hydrochloric acid (or with zinc-powder and ammonia).

<table>
<tr><td colspan="5">Solution decolorised.</td><td rowspan="3">The colour changes to a brownish red. The ammoniacal solution takes its original colour on the filter.</td></tr>
<tr><td colspan="2">Original colour reappears.</td><td colspan="3">Original colour does not reappear.</td></tr>
<tr><td colspan="2">Aqueous solution acidified with HCl and treated with ether.</td><td colspan="3">Colouring matters heated on platinum foil.</td></tr>
<tr><td>Ether dissolves the colour and the aqueous solution is nearly colourless.</td><td>Ether remains colourless.</td><td>Deflagrates without coloured fumes.</td><td colspan="2">Burns slowly with coloured vapours, or deflagrates slightly with coloured fumes.</td><td>Alizarine S.
Alizarine blue S.
Ceruleine S.</td></tr>
<tr><td>Phthaleines.</td><td>Sulphonised derivatives of Rosaniline.</td><td>Nitro colours (Nitrophenoles).</td><td colspan="2">Heat an unmordanted swatch of cotton with aqueous solution.</td><td></td></tr>
<tr><td></td><td></td><td></td><td>Dye bears hot soap.</td><td>Dye does not bear hot soap.</td><td></td></tr>
<tr><td></td><td></td><td></td><td>Benzidine azo dyes.</td><td>Azo dyes.</td><td></td></tr>
</table>

Solid or Pasty Colours, Insoluble in Water.

The dye-wares are treated with water and a few drops of soda-lye at 5 per cent.

The dye-wares dissolve.		The dye does not dissolve.			
The alkaline solution is filtered, zinc-powder is added, heated, and put on filter-paper.		The colouring matters are heated with alcohol at 70 per cent. and dissolve, except indigo.			
Colour of alkaline solution returns.	Colour does not return in the same tone, or original colour is not changed.	Alcoholic solution not fluorescent.		Alcoholic solution fluorescent.	
		Soda-lye at 33 per cent. is added.			
Ceruleine. Galleine. Gallocyanine. Gallofiavine.	Canarine. Alizarine. Anthrapurpurine. Flavopurpurine. Nitroalizarine. Alizarine brown. Alizarine blue. Chrysamine. Solid green. (Dinitroresorcine.)	Colour changes to red-brown.	No change of colour.	Fluoresence disappears.	Fluoresence does not disappear.
		Induline. Nigrosine. Rosaniline blue. Diphenyl-amine blue.	Indophenol.	Magdala red.	Primrose Cyanosine.

Basic Colouring Matters.

Reds: Watery solution bluish red: yellow-brown with HCl and strong sulphuric acid. Sodium acetate restores original colour. Zinc-dust decolorises watery solution; colour does not return. Strong sulphuric acid dissolves it with a yellow-brown. Solid colour green, of metallic lustre *Magenta, Rubine.*

Solution reddish blue; ammonia throws down flocks which dissolve in ether with greenish-yellow fluorescence. HCl turns it blue; sulphuric acid, brownish green; on addition of water, colour turns blue, violet, and lastly red *Neutral Red.*

Alcohol added to the original colour gives orange fluorescence. Zinc-powder decolorises solution. Colour returns on exposure to air. Sulphuric acid makes it green; on dilution with water, passes to blue, violet and red . *Safranine.*

Yellows: Easily soluble in water. With alkalies, a yellow flocky precipitate (brown if impure); soluble in ether with fine yellow colour and strong green fluorescence . *Phosphine (Chrysaniline).*

With alkalies, yellowish-white milky precipitate; soluble in ether *without* colour, and splendid blue fluorescence . *Flavaniline.*

Greens: Easily soluble in water with strong green colour. Alkalies give a rose-coloured or grey precipitate; acids turn it yellow. Sulphuric acid, yellow; green on dilution with H_2O *Malachite Green.*

Soluble in water with a more yellowish-green colour; ammonia gives no precipitate, or a very slight one. Solution of colour in sulphuric acid does not turn green as quickly when diluted with water as does malachite green . *Brilliant Green.*

Soluble in water with a blue or greenish-blue colour. With acids, yellow. Alkalies discharge, but give no precipitate; swatch dyed with this colour turns violet at 100°. Sulphuric acid, yellow; on dilution, green . . . *Methyl Green.*

Violets: Easily soluble in water. Alkalies give a violet

brown solution precipitate, sulphuric acid a yellow, on dilution with water violet blue *Methyl Violet* (Hofmann's).

Sparingly soluble in cold water; HCl turns solution blue; alkalies throw down brown flocks; sulphuric acid turns it a dirty violet *Neutral Violet.*

Not very soluble in water; alkalies give a violet precipitate, sulphuric acid turns colour to grey; on slow dilution with water turns sky-blue, violet-blue, and reddish violet . *Mauveine* (*Rosolane*).

Soluble in water with red-violet colour. Carmine-red fluorescence on adding alcohol. Sulphuric acid, fine green, on dilution becoming blue and then violet *Amethyst* (*Giroflée*).

Soluble in water with very pure tone; HCl turns it orange; soda-lye, a violet-brown precipitate. Strong sulphuric acid, an orange colour, which does not disappear on adding 10 parts of water. Base dissolves in ether with a yellow colour *Crystal Violet.*

Blues: Easily soluble in water; HCl gives the solution a greenish cast. Strong soda-lye, a violet-black precipitate. The colour contains zinc. A 7 per cent. solution of chloride of lime destroys the colour only after the lapse of some hours. Sulphuric acid gives a grass-green *Methylene Blue.*

The watery solution is bluish violet. Strong sulphuric acid gives a green colour which turns blue and violet on dilution. Soda-lye gives a black-brown precipitate. On reduction with Zn and acetic acid, appears first a green colour. Colouring matter a fine powder which causes sneezing . *New Blue B and D.*

There has latterly been sold as "bleu nouveau" a dye the solution of which is violet when hot but green when cold. Alkalies give a red-brown precipitate; HCl a slight blue precipitate. Sulphuric acid gives a violet-red colour, turning violet on dilution; probably a mixture.

Sparingly soluble in cold water, with a violet colour. Tannin gives an indigo-blue precipitate. Sulphuric acid dissolves it bluish green, blue on dilution and then violet; then is formed a precipitate, soluble in much water; soda-lye gives a red-brown precipitate *Muscarine* (Durand & Co.)

Soluble, with a yellow colour. Alkalies give a white milky precipitate. Precipitate soluble in ether without fluorescence. The yellow solution of the dye gradually loses its colour; if boiled with dilute sulphuric acid it becomes colourless. A transient yellow colour on reduction with zinc-powder and acetic acid *Auramine.*

Dyes wool orange-yellow; watery solution of the dye congeals (not always) to a blood-red gelatinous mass. Sulphuric acid dissolves it with a brown-yellow . . . *Chrysoidine.*

Dyes wool a brown-orange; sulphuric acid, a brown; does not gelatinise on cooling *Vesuvine* (*Bismarck brown*).

Moderately soluble in water. Yellow brown with acids; alkalies give a brown-red precipitate; zinc and acetic acid decolorise solution permanently. Sulphuric acid gives a red-brown, turning green-blue on dilution *Victoria Blue.*

Acid Colouring Matters. Phthaleines.

The aqueous solution is pure red with a yellowish-green fluorescence, becoming stronger the more the solution is diluted. Acids throw down orange flocks, soluble in ether with a yellow colour. Strong sulphuric acid dissolves it with a yellow colour; on heating the solution, white fumes of hydrobromic acid escape. With the addition of manganese peroxide, an escape of bromine . . .	*Eosine.*
Watery solution more bluish than that of eosine, and but slightly fluorescent. Acids give a yellow-brown precipitation, which dissolves in ether with a yellow colour. Dissolves in strong sulphuric acid with a golden yellow; on heating, the same phenomena as with eosine. Ammoniacal solution reduced with zinc-powder quickly recovers its colour in the air. If heated on platinum foil, brisk combustion with formation of "Pharaoh's serpents" . .	*Safrosine Scarlet.*
Watery solution bluish red with slight greenish fluorescence. With HCl, a flesh-coloured precipitate which dissolves in ether with a brownish-yellow colour. Sulphuric acid changes the colour to a golden yellow, and on heating this solution hydrogen bromide escapes, or free Br on addition of MnO_2	*Phloxine.*
The watery solution is dark bluish red, not fluorescent. HCl gives a scarlet precipitate, soluble in ether with an orange-yellow colour. The reduced solution is but little oxidised in the air. Dissolves in sulphuric acid with an orange, and, on heating, iodine deposits on the sides of the vessel	*Bengal Rose.*
Solution brownish yellow with strong green fluorescence which disappears on adding HCl with formation of a yellow precipitate	*Uranine, Chrysoline.*
Solution eosine red. HCl gives a yellow precipitate. Strong sulphuric acid gives a yellow precipitate from which neither iodine nor bromine is separated. The watery solution smells of phenol	*Coralline, Aurine.*

Sulphonised Rosaniline Derivatives.

The watery solution is bluish red, colour disappears on heating with soda-lye and reappears on adding acetic acid. Sulphuric acid turns it yellow, red on dilution .	*Acid Magenta.*
Easily soluble in water with slight greenish colour. On the addition of a little acid the colour darkens, but turns yellow with acid in excess. Alkalies discharge the colour	*Helvetia Green.*
Alkalies discharge almost entirely. Wool takes up the colour from an ammoniacal solution. The dyed wool turns deep blue if washed in dilute acid	*Nicholson Blue.*
Easily soluble in water. Wool dyes only in an acidified solution. Alkalies do not precipitate the aqueous solution. Commonly sold in the state of fragments of a metallic lustre	*China Blue.*

Watery solution violet. Ammonia discharges it completely without giving a precipitate. Sulphuric acid turns it orange; on dilution with water, turns green, blue, and at last violet *Acid Violet.*

Soluble in water with a colour varying from blue-grey to red-grey. HCl gives a reddish blue. Alkalies, red or violet. Dilute nitric acid, no change even on heating . *Induline, Nigrosine.*

Nitro Colouring Matters.

Soluble with greenish-yellow colour; solution tastes bitter. Alkalies turn it a dark yellow; no precipitate on adding a yellow to this solution. Colouring matter deflagrates only if mixed with soda *Picric Acid.*

Dissolves with gold-yellow colour. HCl gives a yellowish-white precipitate solution in ether *Martius Yellow.*

Soluble with gold-yellow colour. HCl gives no precipitate. It does not colour ether *Naphthol Yellow S.*

Concentrated aqueous solution red; yellow if dilute; sulphuric acid gives no coloration. Acids turn it yellowish milky; excess of alkalies, a dark-red precipitate. Generally sold as an ammonium salt *Aurantia.*

Benzidine-Azo Colouring Matters.

Watery solutions red; trace of HCl turns it blue. Strong sulphuric acid turns it a slate-blue, and there is no change on diluting with water *Congo Red.*

Watery solution orange red. Strong sulphuric acid or HCl gives a brown precipitate in a concentrated solution; brown solution on diluting *Benzo Purpurine*

Soluble with blue-violet colour; with alkalies, a red solution. Strong sulphuric acid gives it a violet colour. HCl a violet precipitate in strong solution . . . *Azo Blue.*

Solution blue-red. HCl and sulphuric acid, an orange precipitate. Iodine sublimes on heating this colour . *Erythrosine.*

Azo Colours. Yellow-Orange.

Sulphuric acid gives a yellow colour, turning to brown-red and then to orange on dilution. Watery solution yellow. Barium chloride gives a precipitate, but not calcium chloride *Fast Yellow.*

Sulphuric acid turns it violet, red-violet on dilution with immediate formation of a slate-green precipitate. Watery solution yellow; colouring matter separates out in crystals on cooling. Barium and calcium chlorides produce precipitates *Diphenylamine Yellow.*

Watery solution orange; turns violet with HCl. The reduced ammoniacal solution is yellow. Sulphuric acid turns it violet-red, changing to magenta-red on dilution. Sparingly soluble precipitate with barium chloride; no precipitate with calcium chloride *Azoflavine.*

Sulphuric acid colours it yellow, carmine-red on dilution. Watery solution yellow. Colour crystallises out on cooling in yellow scales. Dilute acids precipitate red-violet scales . . . *Methyl Orange.*

Sulphuric acid changes colour to a bluish green, passing on dilution into a violet and depositing a slate-blue precipitate. Watery solution yellow; colouring matter crystallises out on cooling. Barium chloride gives a yellow precipitate which crystallises out from the dilute solution in the form of scales *Yellow N* (Poirrier).

Sulphuric acid turns it a yellow-green, which on dilution becomes violet with a grey precipitate. Watery solution yellow; colouring matter crystallises out on cooling. Calcium chloride gives an orange precipitate, which on heating turns red and crystallises *Luteoline.*

Sulphuric acid gives a carmine colour, which turns yellow on dilution. Watery solution is yellow and often turbid. With an alcoholic solution of soda the colour is red to violet. "Pharaoh's serpents" are formed on ignition . . . *Citronine* (*Curcumine*).

Sulphuric acid turns it deep orange; no change on dilution. Watery solution is orange. With calcium chloride, a finely crystalline salt *Orange G.*

Sulphuric acid dissolves it orange-brown; no change on dilution. Watery solution yellow; on adding a trace of HCl the original solution crystallises out in yellow scales. If more hydrochloric acid is added the crystals appear as grey needles *Tropaoline O.*

Sulphuric acid, a carmine solution; on dilution, an orange precipitate. Watery solution red-orange. Calcium chloride gives a yellow precipitate, which crystallises in red needles on adding an excess of boiling water. Barium chloride yields a sparingly soluble crystalline precipitate . *Orange II.*

Dissolves violet in sulphuric acid; on dilution, brown precipitate and orange solution. Watery solution orange-red, and carmine-red on adding soda-lye *Orange I.* (*Tropæoline 000.*)

Watery solution orange. Hot solution deposits a yellow precipitate on cooling. Sulphuric acid dissolves it yellow. Barium chloride gives a gold-yellow precipitate. Calcium chloride, no reaction *Tartrazine.*

Dissolves of a dirty violet in sulphuric acid, passing into magenta-red on dilution. Watery solution orange. Barium chloride gives a sparingly soluble precipitate . . . *Metanile Yellow.*

Bordeaux Reds.

The strong hot watery solution becomes gelatinous on cooling. Acids precipitate red-brown flocks. Sulphuric acid dissolves it with a green, which on dilution becomes violet-blue and deposits after some time a dirty-brown precipitate *Biebrich Scarlet.*

Calcium chloride throws down a red flocky precipitate which on boiling becomes crystalline and brown-red.

Sulphuric acid changes the colour to an indigo-blue, which on dilution becomes first violet and then red. The reduced ammonical solution of the colouring matter turns yellow in the air *Croceine Scarlet.*

The hot aqueous solution gelatinises on cooling and forms bronzy crystals. Dissolves with a violet colour in sulphuric acid; a brown precipitate on adding water . *Xylidine Ponceau.*

The hot concentrated aqueous solution of the colouring matter on admixture with manganese sulphate deposits, on cooling, long silky crystals of the manganese salt. Sulphuric acid produces a blue colour; wool is dyed a scarlet-red. The ammoniacal solution if reduced no longer becomes yellow on filter-paper *Croceine Scarlet 7B.*

Watery solution a fine red; eosine red in sulphuric acid. Barium chloride gives an almost insoluble precipitate; calcium chloride gives a precipitate gradually . *Ponceau R, 4R and G.*

Watery solution a fine red. Ammonia turns it a red-brown; sulphuric acid, a magenta-red, turning to a pure red on dilution. Barium chloride gives a brown precipitate, soluble with difficulty. Calcium chloride gradually gives a red precipitate *Coccine, Coccinine.*

Solution dark brownish red, as also the dyed wool. Sulphuric acid dissolves it violet, red on dilution. The strong watery solution on the addition of a few drops of strong soda-lye deposits the sodium salt in the form of brown shining scales *Rocceline.*

Watery solution red to claret; barium chloride gives a sparingly soluble precipitate; that with calcium chloride is easily soluble of a brown-red colour. Sulphuric acid dissolves it indigo-blue, red on dilution *Bordeaux G and R.*

The reactions are the same as those of croceine scarlet. The watery solution mixed with ammonia gives a dark violet-red colour. The ammoniacal solution when reduced is re-oxidised again to a yellow on filter-paper . . . *Ponceau S.*

Anthracene Derivatives.

The watery solution is brownish yellow. With HCl, pure yellow; the ammoniacal solution, magenta-red; soda-lye gives a violet colour in the strong solution of the colouring matter; red precipitate with calcium chloride; dissolves of a golden yellow in sulphuric acid; becomes straw colour on solution. Reduced with difficulty *Alizarine S.*

Watery solution olive-brown, ammoniacal solution green. Brown-red solution, obtained by reduction with zinc and ammonia; is very quickly oxidised in the air, with formation of a green precipitate *Coeruleine S.*

Watery solution a brownish-red, becoming green with soda-lye, and greenish blue with ammonia; HCl gives an orange-yellow solution. The solution reduced with ammonia and zinc becomes a brown-red and is easily oxidised in the air. The watery solution must be prepared cold *Alizarine Blue S.*

Colouring Matters Insoluble in Water.

1. Solution in soda-lye is violet ; in sulphuric acid, blue. The colour takes on tissues mordanted with tannin. Met with as a paste or a powder *Gallocyanine.*

Solution in strong soda-lye, indigo-blue ; violet-red on dilution ; in sulphuric acid orange. Met with as a paste *Galleine.*

Soluble in soda-lye with a green colour ; in sulphuric acid, the same. Met with as a paste *Ceruleine.*

Soluble in soda-lye with a dirty yellow ; reduces very badly. Soluble in sulphuric acid with a yellow colour. Met with as a straw-colour paste *Galloflavine.*

2. Insoluble in sulphuric acid ; dissolves in soda-lye with a yellow colour. Dyes unmordanted cotton a fast yellow in a soap-bath. An orange powder . . . *Canarine.*

Soluble in soda-lye with a violet-blue colour ; the alkaline solution mixed with a little zinc-powder turns red without heating ; the paste is orange *Alizarine.*

Solution in soda-lye a magenta-red. Reaction and appearance like alizarine. The above three colouring matters occur mixed, forming the different brands of commercial alizarine *Anthra- and Flavo-purpurine.*

Solution in soda-lye orange ; in sulphuric acid, magenta-red, giving a brown precipitate on dilution. Dyes cotton at once and forms yellowish, brown paste . *Chrysamine.*

Solution in soda-lye is red ; if reduced with zinc-powder it produces deep indigo-blue spots on filter-paper. Forms a yellow paste *Nitro-alizarine.*

Solution in soda-lye orange-brown ; if reduced, produces on filter-paper dark, dirty-brown spots. Dissolves in sulphuric acid with a brownish red *Alizarine Maroon.*

Soluble with difficulty in soda-lye with a green colour ; the reduced solution produces deep-blue spots on filter-paper ; a deep-blue paste *Alizarine Blue.*

3. The alcoholic solution is blue-grey or red-grey. A small quantity of the dry substance heated with a 5 per cent. soda-lye and then extracted with benzene yields a colourless or slightly yellowish solution having a deep reddish-brown fluorescence *Induline, Nigrosine.*

Alcoholic solution deep blue, greenish on adding HCl ; turns brown with soda-lye. No fluorescence with benzol. Dissolves reddish brown in sulphuric acid *Diphenylamine Blue.*

4. Alcoholic solution turns brown-red if mixed with HCl. *Indophenol.*

5. Alcoholic solution bluish red with intense, splendid vermilion fluorescence *Magdala Red.*

6. Bluish red alcoholic solution, with greenish-yellow fluorescence, disappearing on addition of HCl. Colour turns yellow *Primrose.*

Blue-red alcoholic solution has a brick-red fluorescence, disappearing on adding HCl. Colour turns orange . . *Cyanosine.*

7. Pulverised substance, insoluble in alcohol ; reduced with zinc and ammonia, gives a yellow liquid, which produces spots on filter-paper *Indigo.*

SECTION V.

GLASS, EARTHENWARE, CEMENT AND MORTAR.

GLASS MANUFACTURE.

THE manufacture of glass is exceedingly ancient. As the Temple of Belus in Egypt, the age of which is estimated at 12,000 years, was constructed of bricks covered with a glaze, the production of glass cannot be very much less ancient. The composition of certain specimens of glass from Autun, traceable to the second century is, according to Peligot:

SiO_2	.	.	.	.	66·7	...	66·0	...	67·4	...	70·9	...	69·4	...	69·4
CaO	.	.	.	.	5·8	...	7·2	...	2·7	...	7·9	...	6·4	...	7·1
Al_2O_3, Fe_2O_3, Mn_2O_3				.	2·8	...	3·0	...	5·4	...	4·5	...	2·9	...	2·8
Na_2O, K_2O				.	24·7	...	23·8	...	24·5	...	16·7	...	21·3	...	20·7

Composition of Glass.—If we leave out of consideration the glasses soluble in water and varying in composition between $R_2O.2SiO_2$ and $R_2O.4SiO_2$, glass may be regarded as a mixture of silicates obtained by fusion, liquid at high temperatures, becoming pasty as it cools, and finally congealing to a hard, amorphous, and generally transparent mass. The condition is that, besides the compounds of silica (in part replaceable by boric acid) with potassium or sodium, there must be simultaneously present silicates of metals of the calcium, magnesium, or iron group, in order to render the alkaline silicate as far as possible capable of resisting atmospheric and chemical influences. As the lime and lead silicates are chiefly selected to this end, with other metals in case of coloured glass, we can distinguish mainly the following groups:—

(1) Alkaline silicates or soluble glass; (2) Soda-lime silicates or soda glass; (3) potash lime silicates or potash glass; (4) Alkali-lead silicates or lead glass; (5) coloured glass.

If we take the constituents of glass as anhydrides, the simplest formula for soda-glass is $xNa_2O.yCaO.zSiO_2$; in potash glass Na is replaced by K, and in lead glass Pb is substituted for Ca.

Dumas was of opinion that glass has quite as definite a composition as certain minerals, or is at least a mixture of definite silicates; the glasses which he examined gave the proportion of saturation $Na_2O.CaO.4SiO_2$. This formula would indicate for soda glasses the composition SiO_2 67·0 per cent., Na_2O 17·3 per cent., and CaO 15·7 per cent.; for potash glasses 61·6 per cent. SiO_2, 24·1 per cent. K_2O, and 14·3 per cent. CaO, If we compare the composition of good glasses met with in commerce we find that the latter contain much more silica. But since Berthier has shown that an increase of silica renders glass less fusible and harder, whilst lime gives it the power of resisting certain chemical influences, Benrath regards as "glass" also silicates whose saturation answers to the general formula $RO.2SiO_2$. He points out that the most favourable composition for all purposes of the glass manufacture—excepting optical glasses—falls between the boundaries $Na_2O.CaO.6SiO_2$ and $5Na_2O.7CaO.36SiO_2$, where, of course, Na may be replaced by K and Ca by Pb. Hence would follow the subjoined compositions:—

——	SiO_2.	Na_2O.	K_2O.	CaO.	PbO.
$K_2O.CaO.6SiO_2$	70·6	—	18·4	11·0	—
$Na_2O.CaO.6SiO_2$	75·3	13·0	—	11·7	—
$K_2O.PbO.6SiO_2$	53·2	—	13·9	—	32·9
$5K_2O.7CaO.36SiO_2$	71·5	—	15·6	12·9	—
$5Na_2O.7CaO.36SiO_2$	75·5	10·8	—	13·7	—
$5K_2O.7PbO.36SiO_2$	51·6	—	11·2	—	37·2

Composition of Soda Glass.

——	SiO_2.	Na_2O.	K_2O.	CaO.	MgO.	Fe_2O_3.	Al_2O_3.	MnO.	SbO_3.
Window glass, Saarbruck	71·27	12·50	—	14·13	—	1·44	—	—	0·21
„ „ Witten	72·25	13·02	—	13·40	—	1·23		—	0·12
„ „ Stollberg	72·42	12·71	—	13·81	—	0·93		—	0·14
Flask, from Stender, Hanover	73·79	13·94	0·60	8·61	0·12	0·68	0·58	0·32	—
Mirror glass, Münsterbusch	72·31	11·42	—	14·96	—	—	0.81	—	-
Window glass, from „	72·80	12·30	—	14·10	—	0·73		—	—
Combustion-tube, Warmbrunn, Quilitz & Co.	74·06	11·46	3·92	9·71	—	0·98		—	—
White medicine bottles, Rhenish Works	72·07	18·45	—	8·96	—	0·54		—	—
White vessel, from Zwiesel	78·39	13·91	—	7·10	—	0·21	0.24	0·15	—
Cast mirror glass, Dorpat	74·05	10·95	—	12·96	—	1·87		—	—
Beaker glass, St. Petersburg	74·66	10·36	4·32	9·13	—	0·78		—	—
Russian semi-white vessel glass	74·00	17.44	—	7·35	—	0·21	0·20	0·80	—
„ „ „	69·99	17·96	—	9·90	—	0·39	1·11	0·65	—
Venetian window glass	68·60	8·10	6·90	11·90	2·10	1·20	0·30	—	—
White glass, Bagneaux, Nemours	72·00	17·00	—	6·40	—	1·10	2·60	—	—
French medicine bottles	62·00	16·40	—	15·60	2·20	0·70	2·40	—	—
French crown glass, for lighthouses	72·10	12·00	—	15·70	—	trace	trace	—	—
English mirror glass, St. Helens	77·36	13·06	3·02	5·31	—	0·92	trace	—	—
Do., Thames Co., London	78·69	11·63	1·34	6·10	—	trace	2·68	—	—
Do., London & Manchester Co.	77·91	12·36	1·73	4·85	—	—	3·60	trace	—
Window glass, Charleroi, Belgium	74·82	13·01	—	11·21	—	1·03		—	trace
American pressed glass	75·00	18·62	—	5·18	0·52	0·19	0·11	0·38	—

Potash Glass.

——	SiO_2.	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Al_2O_3.	MnO.
White glass, Venice	68·60	6·90	8·10	11·00	2·10	0·20	1·20	0·10
„ Bohemia	71·70	12·70	2·50	10·30	—	0·30	0·40	0·20
Bohemian tubing	74·40	18·50	—	7·20	—	—	0·10	—
„ „	73·13	11·49	3·07	10·43	0·26	0·13	0·30	0·46
„ „	71·60	11·00	—	10·00	2·30	3·90	2·20	0·20
„ mirror	67·70	21·00	—	9·90	—	—	1·40	—
„ average glass	76·00	15·00	—	8·00	—	—	1·00	—
Wine glass, Nortjö, Finland	74·37	12·71	3·42	9·02	—	0·71		—
Mirror, Dorpat	62·29	21·12	6·78	6·50	—	3·25		—
Russian beer glass	73·90	12·55	6·90	5·65	—	0·90		—

	SiO_2.	K_2O.	Na_2O.	CaO.	PbO.	Fe_2O_3.	Al_2O_3.	MnO.
Crystal glass, Bonèche	56·00	6·60	—	—	34·40	—	1·00	—
" from London for chemical apparatus	59·20	9·00	—	—	28·20	0·40	—	1·0
" from Newcastle	51·40	9·40	—	—	37·40	2·00		—
" from Baccarat	51·10	7·60	1·70	—	38·30	1·30		—
French lamp glass	48·10	12·50	—	0·60	38·00	0·50	—	—
Flint glass, Guinaud	42·50	11·70	—	0·50	43·50	—	1.8	As_2O_5 trace
" Waldsteien, Vienna	75·24	12·51	—	1·48	10·48	trace	trace	—
French pressed glass	50·18	11·62	—	—	38·11	trace	0·14	trace
English " "	61·27	7·07	7·55	1·05	22·36	—	0·86	—

Schott made a number of experiments, giving glasses of the following compositions :—

—	I.		II.		III.		IV.		V.		VI.		VII.		VIII.	
	Mol.	p.c.	Mol.	p.c.	Mol.	p.c.	Mol.	p.c.	Mol.	p.c.	Mol.	p.c.	Mol.	p.c.	Mol.	p.c.
SiO_2	2	50·4	3	60·4	4	67·0	5	71·8	6	75·3	3	50·0	4	57·1	5	62·4
CaO	1	23.6	1	18·8	1	15·6	1	13·4	1	11·7	1	15·6	1	13·3	1	12·6
Na_2O	1	26·0	1	20·8	1	17·4	1	14·8	1	13·0	2	34·4	2	29·6	2	26·0

The glass I. was completely devitrefied on slow cooling; II. chiefly, and III. (which answers to the formula of Dumas) but little; IV., which corresponds to the formula $Na_2O.CaO.5SiO_2$, was very good. Sample V. could be melted only with great difficulty; VI. was half devitrified; VII. and VIII. were apparently good, but would have been too little resistant. Schott believes that no single unitary formula can be proposed for all glasses in common use. Window glass may answer to the above formula, $Na_2O.CaO.5SiO_2$; mirror glass must contain more silica, but less lime; and glass for vessels, bottles, &c., more lime.

R. Weber gives the following analyses of good glasses :—

SiO_2.	Al_2O_3.	CaO.	MgO.	PbO.	K_2O.	Na_2O.	In all.	SiO_2–CaO–Na_2O.
71·23	1·70	16·39	0·20	—	—	10·78	100·30	4·0–1–0·60
71·03	2·98	15·62	0·15	—	—	10·76	100·54	4·2–1–0·60
71·92	0·85	13·65	0·16	—	—	13·42	100·00	4·8–1–0·88
73·35	0·73	11·91	0·71	—	—	13·12	100·00	5·3–1–0·90
72·68	1·06	12·76	0·26	—	—	13·24	100·00	5·2–1–0·90
72·66	0·95	15·20	0·25	—	—	10·94	100·00	4·4–1–0·60
70·58	1·01	16·07	0·80	—	—	11·77	99·23	3·8–1–0·60
74·58	1·23	5·57	0·14	0·34	17·90	—	99·76	12·5–1–2·00
75·81	1·01	7·38	0·10	—	11·39	4·84	100·53	9·6–1–1·50
72·13	1·41	11·51	—	—	5·66	10·06	100·77	5·8–1–1·00
75·23	2·12	8·00	0·03	—	6·38	8·84	100·60	8·8–1–1·50
70·07	1·02	12·13	0·32	—	15·03	2·00	100·57	5·2–1–0·85
53·70	1·12	0·17	—	37·02	7·36	0·70	100·07	5·3–1–0·50
53·70	1·07	0·59	—	34·91	9·12	0·30	99·69	5·3–1–0·60
52·41	0·96	0·77	—	35·24	10·37	0·08	99·83	5·1–1–0·64
45·24	0·82	0·36	—	47·06	6·80	—	100·28	3·5–1–0·33

Glass when in a state of full fusion dissolves metals (gold, copper, silver, lead), oxides (SnO_2, Cr_2O_3, Al_2O_3, Fe_3O_4, Mn_3O_4,SiO_2, CaO), and salts (calcium phosphate, aluminium fluoride, sodium sulphate), and if quickly cooled forms a homogeneous, amorphous mass. If cooled slowly a part of the dissolved matter separates out either in crystals or in an amorphous state. Even the excess of alkali seems to be merely in a state of solution. Glass melted with alkali corresponds to the same saturation; it dissolves at high temperatures up to 84 per cent. of silica in excess, which on slow cooling separates out again.

Calcium in glass can be substituted by a series of other elements. Thus on melting together—

	I.		II.
Sand	250	...	250
Sodium carbonate . .	100	...	100
Magnesia	50	...	50
Calcium carbonate . .	—	...	60

Pelouze obtained the following glasses:

SiO_2	68·9	...	65·7
Na_2O	16·2	...	15·0
MgO	14·9	...	12·0
CaO	—	...	7·3
Specific gravity .	2·47	...	2·54

These glasses are very fusible and readily become devitrified, especially II.

Whilst compounds of barium and strontium have often been added to mixtures for glass, Benrath has shown that apparently the alkali can be replaced by baryta, as the following analyses of three specimens of glass show, of which III. had been prepared at St. Gobin, according to Peligot:—

	I.		II.		III.
SiO_2 . . .	44·93	...	54·69	...	46·5
CaO . . .	6·61	...	17·06	...	6·3
BaO . . .	44·98	...	24·51	...	47·2
$Al_2O_3.Fe_2O_3$. .	3·48	...	3·74	...	—

But these glasses, scarcely corresponding to the saturation $RO.2SiO_2$, are rapidly attacked even by dilute mineral acids, and are consequently quite useless. The following glass, (I.) was good; its composition approximates to the equivalent proportion:

$$Na_2O.CaO.BaO.9SiO_2.$$

	I.		II.
SiO_2	65·14	...	74·19
Na_2O	9·37	...	17·02
CaO	5·29	...	2·88
PbO	—	...	0·86
BaO	17·18	...	5·16
$Al_2O_3.Fe_2O_3$. . .	2·57	...	0·58
SO_3	0·45	...	0·28

II. is the analysis of a good English compressed glass, of the sp. gr. 2·524. A good barium lead glass is made at Mastricht with witherite, corresponding to the formula $4K_2O.2BaO.3CaO.3PbO.36SiO_2$, and is mentioned by Benrath in support of his formula.

We may notice the attempts of Lamy to introduce thallium into glass. From 300 parts sand, 400 thallium carbonate and 100 parts potassium carbonate or 300 sand, 200 red lead, and 335 thallium carbonate, he obtained an easily fusible, quite homogeneous glass of sp. gr. 4.235, and with an index of refraction for the yellow ray of 1·71; finally he succeeded in obtaining a glass of sp. gr. 5·625 and a refractive index of 1·965.

On the other hand, calcium may be in part replaced by zinc; a very good glass for optical purposes by Maes, of Clichy, has the following composition:—

SiO_2.	ZnO.	PbO.	Fe_2O_3 and Al_2O_3.	CaO.	As.	Alkali and Boric acid.
56·61 ...	13·50 ...	4·10 ...	0·40 ...	0·70 ...	trace ...	24·69

Bottle glass, prepared from very impure materials, can only approximately correspond to the normal formula, on account of its high percentage of ferric oxide and

alumina, as it appears from the composition of good bottles. If the proportion of alumina, lime, and alkali exceeds a certain limit the glass becomes less capable of resisting water and acids, and is consequently useless. The following analyses of bottles which have proved bad in practice show that the proportion of the ingredients of glass cannot be made to vary very widely:—

Analysis of Bottles.

	SiO_2.	Na_2O.	K_2O.	CaO.	MgO.	Fe_2O_3.	Al_2O_3.	MnO.	SO_3.
Good wine bottles, Souvigny	60·00	3·10	—	22·30	—	4·00	8·00	1·20	—
„ „ St. Etienne	60·40	3·20	BaO 0·90	20·70	0·60	3·80	10·40	—	—
„ „ Epinac	59·60	3·20	—	18·00	7·00	4·40	6·80	0·40	P_2O_5 0·40
Good Champagne bottle	58·40	9·90	1·80	18·60	—	8·90	2·10	—	—
Bottle glass, Follembray	61·35	2·80	2·01	24·66	—	5·51	3·67	—	—
„ Montplaisir	66·04	2·83	2·82	22·88	—	2·78	2·65	—	—
French bottle, attacked by wine	52·40	—	4·40	32·10	—	6·00	5·10	—	—
English do., do.	49·00	7·25	2·00	24·75	2·00	10·00	4·10	trace	—
Good English wine bottle	59·00	10·00	1·70	19·90	0·50	7·00	1·20	—	—
Do. at Paris Exhibition	53·25	4·25	—	25·50	2·00	15·0		—	—
Swedish bottle, meted with fluor-spar	55·20	6·99	2·85	15·40	1·08	3.60	11·00	2·79	F 1·75
Bottle from Siemens, Dresden	63·91	7·05	—	14·52	—	13·97			0·55
Water bottle, bad	69·55	13·61	0·41	15·09	0·42	0·33	0·42	—	—
Do., attacked by water	70·12	13·01	0·42	14·94	0·38	0·39	0·37	—	—
Do., corroded	72·63	14·86	—	9·92	—	2·07		—	trace
Dull window pane	69·37	21·11	—	7·54	—	1·55		—	0·40
Opaque glass	73·64	16·54	—	7·85	—	1·59		—	0·38
Opalescent mirror glass	73·70	17·18	—	6·53	—	1·89		—	0·70
Spotty window glass	66·47	5·61	18·79	5·60	—	3·10		—	—

Lime-Alumina Glass.—Pelouze has attempted the production of an alumina-glass without arriving at results of importance. Korschelt recommends the production of a white glass from alumina, silica, and lime. As raw materials he takes the kaolin of Meissen (consisting of 77 per cent. silica, 18 per cent. alumina, and 5 per cent. water) along with a calc-spar free from iron burnt lime. Quartz is added only if the kaolin does not contain sufficient silica. The mixture is regulated so that it consists of 55–67 silica, 10–18 alumina, and 15–35 lime. A mixture of 100 parts Meissen kaolin and 41 parts burnt lime would, *e.g.*, contain 55·2 per cent. silica, 14·2 alumina, and 30·6 per cent. lime. The lime of the mixture can be partially or entirely substituted by baryta or magnesia. Magnesia makes the mixture less fusible but permits of the use of magnesian limestones, dolomite, &c.

Phosphatic Glass, obtained from fused calcium phosphate, is recommended for vessels which have to come in contact with hydrogen fluoride.

Solubility of Glass.—Whilst Boyle (1664) and Margraf were of opinion that earth could be produced from pure water by continued distillation, Kunkel (1744) and Scheele and Lavoisier (1770) were aware that glass is more or less dissolved by water. Glasses rich in alkali become damp on exposure to the air, gradually lose their lustre, become semi-transparent, and have sometimes an iridescent surface. The same phenomena occur if glass has been placed for a long time in water or moist earth: the water extracts the alkalies, the surface loses its compactness and exfoliates. According to Hausmann, a glass thus decomposed had the following composition:—

	SiO_2.	Al_2O_3.	CaO.	MgO.	FeO.	Na_2O.	K_2O.	H_2O.
Undecomposed part	59·2	5·6	7·0	1·0	2·5	21·7	3·0	—
Decomposed surface	48·8	3·4	11·3	6·8	11·3	—	—	19·3

The decomposition by water increases rapidly with the rise of temperature. Griffith found that on slow ebullition water extracted from flint glass 7 per cent.; the solution contained no lead.

According to Pelouze two samples of glass of the following compositions:—

	I.	II.
SiO_2	72·1	77·3
CaO	15·5	6·4
Na_2O	12·4	16·3

when powdered and boiled in water, lost, I., 10 per cent.; and II., 32 per cent. The solution contained basic silicate and always a little sulphate. Powdered glass on exposure to the air slowly absorbs carbon dioxide and at once exerts an alkaline reaction with litmus paper. Benrath digested 16 parts powdered glass for three days and obtained in the solution 0·193 parts of the following composition:—

	SiO_2.	CaO.	Na_2O.	Al_2O_3.	SO_3.	Ca_2.
Glass used	76·27	6·09	16·38	0·63	trace	—
Residue	28·43	—	47·39	—	0·18	24·00

Here a strongly basic alkaline silicate had been extracted. When Daubrée treated glass with superheated steam under pressure it was completely resolved into silica, Wollastonite ($CaSiO_3$), and alkaline silicate.

Emmerling shows that the loss of weight of a glass vessel by the action of liquids depends on the time of boiling, the size of the surface wetted, its condition, the composition and the concentration of the solution. The speed of evaporation is not essential. The composition of the glasses examined was—

	a.	*b.*	*c.*	*d.*
SiO_2	73·79	72·69	74·14	79·57
Al_2O_3	0·58	0·63	1·15	0·35
Fe_2O_3	0·68	0·97	0·68	0·24
MnO	0·32	0·54	0·49	—
CaO	8·61	9·20	6·94	7·18
MgO	0·12	0·34	0·24	0·18
Na_2O	13·94	12·83	15·07	3·45
K_2O	0·60	1·77	0·60	8·04
	98·64	98·97	99·31	99·01

In experiments with glass flasks containing 600 to 700 c.c. of the first sort of glass, using 400 c.c. of the liquid in question and replacing the water lost by evaporation, there was found on boiling with pure water in the first hour a decrease of weight of 3·9 milligrammes; in the second, 2·7 milligrammes, and during the following twenty-eight hours losses of 2·5 to 1·5 milligramme. Hydrochloric acid at 11 per cent. dissolved in the first hour 4·2 and 5·3 milligrammes; in the following only 0·9. Hydrochloric acid of 0·2 to 3 per cent. dissolved scarcely anything. The action increases thus both with greater dilution and with greater concentration; 0·008 per cent. nitric acid counteracts the solvent power of water; 1 per cent. dissolved 3 milligrammes. Sulphuric acid from 0·25 to 25 per cent. dissolves hourly about 3·8 milligrammes, and 1 per cent. oxalic acid dissolves 0·1 and 0·2 milligramme. Alkaline liquids attack glass especially readily.

From these researches it appears that in accurate work no new glass vessels should be used, that liquids should be boiled in them for as short a time as possible. Alkaline solutions, even if dilute, should not be heated in glass vessels.

Kreusler calls attention to analytical errors which may be occasioned by the alkaline reaction of glass. In order to determine the behaviour of different sorts of glass with water, glass tubes were fixed in the necks of small boiling-flasks containing about 50 c.c. of water in such a manner that on boiling they might act as reflux condensers. The contents of the flasks were then titrated and the result calculated for nitrogen (in determinations of ammonia), and in caustic alkali. For 1000 square centimetres of surface attacked the result was hourly, if calculated for the first two to three hours:

Thuringian glass, 1	24·0
„ „ 2	3·2
Bohemian combustion tube	0·3
Fusible potash glass	0·5

calculated in milligrammes nitrogen. On the basis of the entire duration of the experiment the loss was reduced in the first two cases respectively to 9·5 and 2·04 milligrammes nitrogen. With the other two kinds of glass the result was not altered.

According to the experiments of Stass, glasses rich in silica and free from alumina stand best. A glass of the following composition totally resisted the attacks of acids and dilute alkalies:—

SiO_2.	K_2O.	Na_2O.	CaO.
77·0 ...	7·7 ...	5·0 ...	10·3

Weber and Wiebe show that glass intended for the manufacture of thermometers should contain as alkali only soda, or only potash. To test the resistance of glass Weber exposes the articles to the fumes of hydrochloric acid. Good glasses when dried should show no coating.

Devitrification.—As far back as 1727 Reaumur observed that glass exposed for some time to a temperature at which it softens but does not melt becomes dull, opaque, and of a milky white. Opinions still differ on the cause of this phenomenon. Dumas and Peligot hold that definite silicates crystallise out of the glass, leaving the rest as a kind of mother liquor. Glasses rich in silica are most easily devitrified.

Coloured Glasses.—Combustion tubes used in organic analysis sometimes take a fine red colour. If glass is coated with a mixture of copper oxide and some adhesive matter, and ignited, it takes up copper, but remains colourless. On heating in hydrogen or any other reducing glass it becomes a fine red. More beautiful is the "copper ruby" obtained by fusion. If glass is melted with 1 per cent. copper oxide, on adding 2 per cent. of tin or 1½ per cent. forge-scales, there is obtained a glass which is colourless or merely greenish, but if it is heated to the point of softening it suddenly takes an intense red, the well-known colour of old church windows. Copper ruby contains 0·42 to 0·66 of metallic copper. If the proportion is increased glass takes up 6·75 per cent. copper as a maximum and then becomes opaque.

Hematinon.—This is a glass resembling that found in the Pompeiian excavations, and mentioned by Pliny. It posesses a beautiful red colour, between that of vermilion and of minium, is opaque, harder than ordinary glass, bears a high polish, and has a sp. gr. = 3·5. The colour is lost by melting, and by no addition can be recovered. The glass contains no tin or cupreous oxide as a colouring matter. Von Pettenkofer assimilated to this glass by melting together silica, lime, burnt magnesia, litharge soda, copper-hammerings, and smithy scales. A part of the silica in the mixture is decomposed by means of boric acid, and a mass is obtained which, when ground and polished, exhibits a dark red colour of great beauty. Pettenkofer gave to this glass the term astralite, from the beautiful shotte-colour of blue or dichromatic tint shimmering throughout the mass.

By a somewhat similar process we obtain *Aventurine.*

Aventurine Glass.—Aventurine or avanturin glass was formerly made only in the

Island of Murano, near Venice, but is now prepared throughout Germany, Italy, Austria, and France. It is a brown glass mass in which crystalline spangles of metallic copper according to Wöhler (of cuprous oxide according to Von Pettenkofer) appear dispersed. Fremy and Clemandot have produced a glass similar to aventurine glass, and which consisted of 300 parts glass, 40 parts cuprous oxide, and 80 parts copper scale. The Bavarian and Bohemian glass houses produce an aventurine glass rivalling the original. Von Pettenkofer has prepared aventurine glass direct from hematinon by mixing sufficient iron-filings with the molten mass to reduce about half the copper contained. Pettenkofer surmises, and with good reason, that aventurine glass is a mixture of green cuprous oxide glass with red crystals of cuprous silicate, these complementary colours giving the brown tint. This glass is also well imitated by melting a mixture of equal parts of ferrous and cuprous oxides with a glass mass. The cuprous oxide appears after a long annealing as a separate crystalline red combination, while the ferrous oxide is lost in the green colour it imparts to the glass. Pelouze found that by freely adding potassium chromate to the glass materials spangles of chromium oxide were separated. He termed this glass chrome-aventurine; it has been employed by A. Wächter in the glazing of porcelain.

The production of gold ruby glass was known to Neri (1612) but it was first brought under full control by Kunckel. According to the researches of Müller and Knapp, glass dissolves only a small proportion of metallic gold; 20 milligrammes of gold are sufficient to give a uniformly fine colour to 1 kilo. of lead glass; other glasses are less readily treated. If the glass is cooled quickly, the metallic gold is like copper in a colourless state, and on reheating changes into the coloured variety.

Glass with a mixture of fine silver oxide or silver chloride, coated over with clay and water and heated in a muffle, takes a fine yellow colour. According to Bontemps this sometimes takes place in the cold. Metallic silver dissolves in glass, which takes yellow or orange shades. From 8 to 92 milligrammes metallic silver ore, metallic lead, and antimony oxide do not impart any colour to glass.

Ferric oxide, known commercially as blood-stone, ochre, or red chalk, is also used to impart a red colour. Yellow and topaz-yellow are obtained by means of potassium antimoniate or glass of antimony, silver chloride, silver borate, and by silver sulphide. Uranium oxide imparts a green-yellow. Blue is obtained from cobalt oxide, more seldom by means of copper oxide. Green results from the addition of chromium oxide, copper oxide, and ferrous oxide. Violet is obtained from manganese oxide (braunite) and saltpetre; black, from a mixture of ferrous oxide, copper oxide, braunite, and cobaltous oxide. A beautiful black results from iridium sesquioxide.

Alkaline polysulphides turn glass a fine red. Glass coloured yellow with sulphur is especially adapted for windows, glass shades, &c., for protecting sensitive objects from light. Pelouze considers that the reason why many glasses turn yellow on prolonged exposure to light is that sulphates present are reduced to sulphides. He observes that selenium gives glass an orange-red colour. Uranium gives glass a green or a yellow colour. It is, like sulphur, often used where the chemically active rays of light are to be excluded. Reference is made to the fluorescent properties of light-green uranium glass. As fluorescent substances convert the chemical light-waves into the luminous, it is very probable that the utility of uranium glass depends not upon the optical characters of yellow colours, but upon their transforming power.

Venetian mosaic glasses have been examined by H. Schwartz. Their composition was—

—	Chrome-yellow.	Grey.	Carmine.	Vermilion.	Blue.	Purple.	Orange.	Blue.	Violet.	Purple.	Carmine-black.
SiO_2	51·74	48·80	46·95	52·68	62·48	58·00	29·20	57·20	52·08	52·40	52·20
Sb_2O_5	7·91	13·47	1·42	—	—	5·47	4·00	3·55	3·15	5·26	5·89
As_2O_5	—	—	9·96	7·84	—	2·33	1·95	0·66	4·29	2·35	0·56
PbO	19·94	9·99	18·98	16·52	9·86	6·74	56·45	5·95	9·53	4·04	5·37
Cu_2O	—	—	—	—	—	—	—	2·25	0·22	—	—
CuO	—	—	—	—	—	—	—	(2·51)	—	0·10	0·31
CoO	—	—	—	—	0·20	—	—	0·51	0·09	0·15	0·36
FeO	—	—	—	—	—	—	—	—	—	—	—
Fe_2O_3	0·70	0·70	0·63	0·30	1·49	0·60	2·02	0·90	0·76	1·60	1·55
MnO	0·42	—	—	—	—	—	—	4·49	—	—	—
Mn_2O_3	—	—	0·15	0·15	—	trace	2·91	(5·02)	5·28	11·50	11·45
CaO	4·42	11·85	3·80	4·50	2·99	5·20	1·50	7·64	4·97	7·61	7·30
MgO	0·91	1·45	1·40	0·81	—	0·38	0·36	1·12	0·86	0·86	1·98
Ka_2O	2·26	—	9·99	10·15	7·85	9·96	1·41	5·26	9·59	1·41	4·90
Na_2O	12·83	13·12	5·43	4·69	13·75	9·29	—	9·39	8·57	11·89	8·54
Au	—	—	trace	—	—	0·10	—	—	—	—	—
Bo_2O_3 and loss	—	—	1·29	2·40	—	1·93	—	—	—	—	—
	101·13	100·52	100·00	100·00	98·82	100·00	90·90	98·92	99·39	99·17	100·41

Physical Properties of Glass.—Glass is so completely impervious that according to Quincke no ponderable quantities of carbon dioxide or of hydrogen escape through it even in 17 years and at pressures ranging from 40 to 126 atmospheres. The sp. gr. of alkali lime-glasses varies from 2·4 to 2·6; that of alkali-lead glasses from 3·0 to 3·8, and that of thallium glasses may reach 5·625. The sp. gr. is increased by cooling. Thus, according to Riche flint glass after cooling has a sp. gr. of 3·610. The linear expansion of glass on heating from 0° to 100° is 0·0007 to 0·0009.

The power of glass to refract light seems to decrease where the proportion of silica and alumina is high, and to increase very considerably with a rising percentage of lead.

Glass is a bad conductor of heat and electricity, though glasses which are rich in alkali, and consequently hygroscopic, are not good insulators. A glass from Glasgow, distinguished for its insulating power, has the following composition:—

SiO_2.	K_2O.	Na_2O.	PbO.	CaO.	MgO.	Fe_2O_3.
58·45 ...	9·24 ...	3·74 ...	28·02 ...	0·06 ...	0·05 ...	0·47

In consequence of its low conductivity for heat, glass breaks readily if suddenly cooled or heated, especially if it has been imperfectly annealed. If too suddenly cooled the external layers contract whilst the internal mass is still hot and soft, so that on further refrigeration a tension occurs which shatters the glass on the slightest contact, and sometimes apparently even without any external cause. This is the case with the so-called glass tears and with Bolognese phials, small flasks which have been cooled rapidly and which burst if scratched with a grain of sand.

Glass is flexible only in fine threads, so that it can even be felted. In larger pieces it is always brittle. The statement that glass becomes flexible by prolonged burial in the earth and resumes its brittleness on exposure to the air seems incredible. Glass is tolerably resistant to steady pressure. Glass tubes bear an internal pressure of 120 kilos. per square centimetre. The resistance of glass globes is somewhat less. According to other experiments the crushing strain of flint-glass is 1700 kilos. and the resistance to rupture 180 kilos; that of bottle-glass is 200 kilos. A small glass of 1 millimetre thickness of glass resisted, according to Cailletet, an external pressure of 460 atmospheres, but burst with an internal pressure of 140 atmospheres.

Raw Materials used in Glass Making.—These are:—1. Silica, viz., quartz, for very pure glass; for other kinds sand of varying quality, or pulverised flint stones. For very pure glass the silica ought to be free, or very nearly so, from iron; in some cases the

ferric oxide adhering to the quartz or mixed with the sand is removed by hydrochloric acid; while the sand is always first ignited, and in some instances previously washed, to remove clay, marl, humus, &c. Ordinary glass is made with coarser materials; the sand is not required to be so pure, as when it contains lime, chalk, or clay, it renders the mass more fusible.

2. Boric acid is sometimes used as a substitute for a portion of the silica. It increases the fusibility of the glass, imparts to it a high polish, and prevents devitrification. It is employed as borax or as boro-calcite, a native boric acid.

3. Potassa and soda are used in a variety of forms, the former chiefly as potash (potassium carbonate), or partly lixiviated wood-ash.

Not so large a quantity of soda is required as of potash; 10 parts of sodium carbonate correspond to 13 parts of potassium carbonate. Recently the soda has been used in the form of Glauber's salt; in this case, so much carbon is added to the siliceous earth and Glauber's salt as will reduce the sulphuric acid of the sodium sulphate to sulphurous acid, and the carbon to carbon monoxide. The silicic acid then easily decomposes the sulphurous acid of the sulphite. To 100 parts of Glauber's salt (anhydrous) 8 to 9 parts of coal are measured. An excess of carbon is detrimental, as a large quantity of sodium sulphide is formed, which imparts a brown tint to the glass.

4. The lime used in glass-manufacture must be free from iron. It is generally employed as marble or chalk, either raw or burnt. To 100 parts by weight of sand, 20 parts by weight of lime are added. In the Bohemian manufacture the lime is employed as neutral calcium silicate, Wollastonite, SiO_2Ca. Instead of lime, strontia and baryta can be used, the former as strontianite ($SrCo_3$), the latter as witherite ($BaCO_3$). Fluor-spar ($CaFl_2$) and sodium aluminate were at one time used in making milky or semi-opaque glass.

5. Lead oxide is employed in most cases in the form of minium or peroxide, giving up some of its oxygen to form a lower oxide, and purifying the glass. The lead gives the glass a higher specific gravity, greater brittleness, transparency, and polish. It must be free from copper and tin oxides, the former imparting a green colour, and the latter an opacity to the glass. White-lead is as efficacious as red-lead, provided no heavy-spar be present.

6. Zinc oxide is always added as zinc-white. When the colour is not of importance, zinc-blende with sand and Glauber's salts may be used.

7. Bismuth oxide is only added in small quantities in the preparation of glass for optical instruments. Bismuth may be employed either as oxide or nitrate.

The natural silicates are only employed alone in the manufacture of bottle-glass; some of the preceding additions are requisite in clear glass manufacture.

Bleaching.—Coloured glass as it occurs in the first processes of manufacture may have the colour disguised by mechanical mixture with white glass, or the colour may be discharged by chemical agents. Such agents are usually—braunite, arsenious acid, saltpetre, and minium or red-lead.

1. Braunite MnO_2, has long been used as material for glass-clearing. This oxide of manganese is, however, used only in small quantities; too much imparts a violet or amethyst-red colour to the glass; while an excessive amount renders the glass dark-coloured and opaque. The violet-coloured glass is generally prepared with manganese silicate by the addition of braunite to colourless glass. The action of braunite in clearing glass or rendering it colourless has been variously explained. It may be considered that there arises in the molten glass the colours complementary to white, that is, the green from iron silicate and the violet from manganese silicate. This view is supported by the experiments of Körner, who obtained a colourless glass from a mixture of red and violet glasses; and further by those of Luckow, who

obtained a colourless glass by the melting together of a glass strongly tinted red by manganous oxide with copper oxide. The glass-blowers of the Bavarian Forest assert that a rose-red quartz there found is equalled by no other quartz in the production of the best crystal or clear glass. Von Fuchs says that this quartz contains 1 to 1·5 per cent. of titanium oxide, which, similarly to Braunite, effects the chromatic neutralisation. Kohn employs for this purpose nickel or antimony oxide. Zinc oxide has lately been employed to remove or mask the green colour of glass, also imparting a higher polish. 2. Arsenious acid effects the removal of colour by chemical means only from glass containing carbon or iron silicate: in glass containing carbon—

$$\left.\begin{matrix}\text{Arsenious acid, } As_2O_3\\ \text{Carbon } 3C\end{matrix}\right\} \text{ give } \left\{\begin{matrix}\text{Arsenic, } As_2,\\ \text{Carbon monoxide, } 3CO;\end{matrix}\right.$$

in glass containing ferrous oxide:—

$$\left.\begin{matrix}\text{Ferrous oxide, } 6FeO\\ \text{Arsenious acid, } As_2O_3\end{matrix}\right\} \text{ give } \left\{\begin{matrix}\text{Ferric oxide, } 3Fe_2O_3,\\ \text{Arsenic, } As_2.\end{matrix}\right.$$

The arsenious acid is reduced by the carbon and ferrous oxide at a dull red heat, while the arsenic is volatilised.

3. Saltpetre is added chiefly as Chili-saltpetre or sodium nitrate. In the manufacture of lead-glass (flint-glass) lead nitrate is substituted for the sodium nitrate. Barium nitrate has recently been employed to discharge the colour of glass; its action is similar to that of arsenious acid.

4. That minium serves to render glass colourless has already been noted. Chambland states that glass may be whitened by forcing through it while molten a stream of air.

Utilisation of Refuse Glass.—The materials of glass manufacture are never melted alone, but always with nearly the third part of prepared or finished glass. For this purpose, pieces of broken glass, flaw glass, the hearth droppings, and the glass remaining adherent to the blowers' pipes may be utilised—serving a purpose in the manufacture of glass similar to the rags in paper-making. Thus there is only a very small loss of materials. At each re-melting, however, a portion of the alkali of the fragmentary glass is volatilised, and must be replaced by the addition of an alkaline salt.

A proportion of old broken glass, known in the trade as "cullet," is added to the materials for glass-making, sometimes to the extent of one-third.

Melting Vessels.—The vessels in which the glass is melted are placed immediately upon

Fig. 402.



Fig. 403.

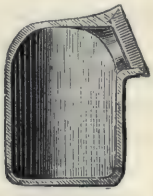


Fig. 404.

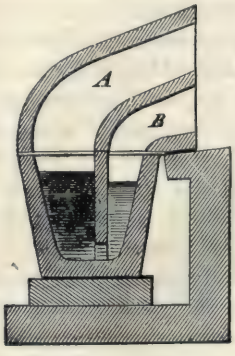
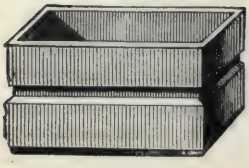


Fig. 405.

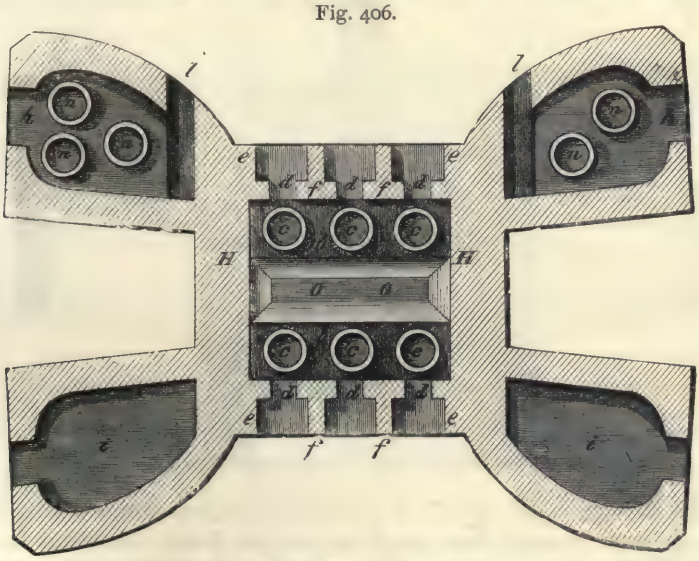


the hearth, and are made of difficultly-fusible clay and powdered old broken melting-pots. They are usually 0·6 metre in height, the walls being 9 to 12 centimetres thick. They

are dried in a temperature of 12° to 15°, and then placed in a chamber heated to 30° to 40°. After remaining about a month, the vessel is put into the tempering or annealing oven, heated to 50°; it is next removed to the ordinary melting-oven, and gradually heated to the melting-point of glass, at which it remains for three to four hours. When a new pot is first used for glass-melting, the alkaline constituents of the glass act upon the clay, forming a rich clay glaze or glass, which, if allowed to mix with the ordinary glass, would be highly detrimental. Consequently broken glass and refuse are first melted in the vessel, and the glaze imparted, termed technically the lining, is a sufficient protection to the glass in after-practice. The shape of the melting vessels varies. For melting with wood or gas the conical form, Fig. 402, is employed. When coal is used as fuel, the vessel takes the covered form, Fig. 403. Fig. 404 represents a rather peculiar form; the glass constituents are melted in *A*, the clear molten glass passing by the aperture in the central wall into *B*. The glass in *B* is thus always free from glass-gall or impurities, which remain behind in *A*. In the manufacture of looking-glasses, large quadrangular vessels, Fig. 405, are employed for refining purposes.

The Glass-furnace.—The glass-ovens are respectively:—1. The melting-oven. 2. The tempering- or annealing-ovens, used in the after-manufacture. The melting-oven can only be made of fire-proof clay. It is built of a mixture of white clay and burnt clay of the same kind. Ordinary mortar and cements are useless for this purpose, on account of their fusibility; therefore the same clay as is used for building is also used for binding. The oven must be built on dry ground; if built on damp ground it is difficult to maintain the lower parts at a constant heat, requiring a larger supply of fuel. The arch is closed with a single piece of fire-proof clay, weighing 800 to 1000 cwts. After building, the oven is dried for four to six months at a temperature

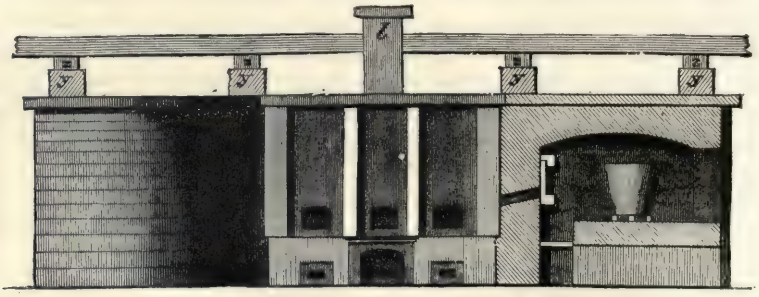
Fig. 406.



of 12° to 15°. A low fire is then lighted, and the temperature gradually increased for about a month until the oven is fit for actual work. The arch is further covered with massive backstones, and these again are covered to a thickness of 5 to 6 inches with a lime-mortar. When much in use, and if not built of very good clay, an oven will not remain in working order for longer than 1¼ to 1¾ year; but if fire-clay is used, and only easily-fusible lead-glass is manufactured, the oven may last for four to five years. The oven contains six or eight to ten melting-pots, which must all be raised to the same temperature. Further, the melting-pot is placed over half the fire-room. The annexed woodcut, Fig. 406, is a ground plan of a complete oven. Fig. 407 is a sec-

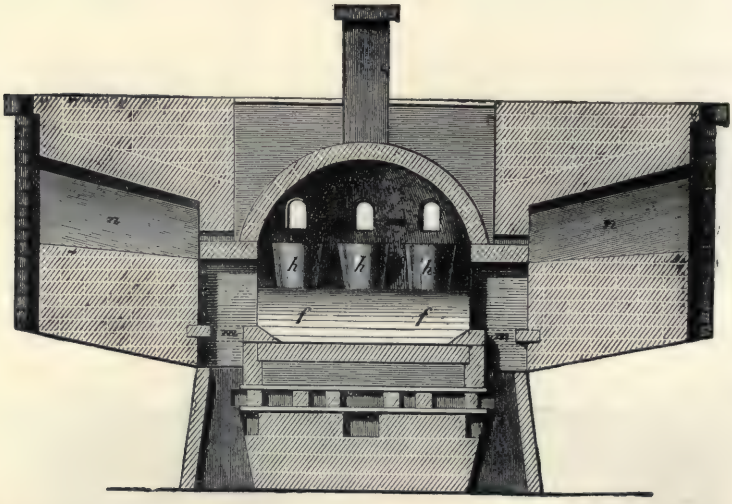
tion showing the melting-ovens and work-holes; Fig. 408 a vertical section through the length of the oven; Fig. 409 a vertical section of the breadth. In the ground plan, Fig. 406, *o o* is the flue; *c c c* are the melting-pots; *n n*, pots containing glass in another stage of preparation; *d d d*, the work-holes; *b b*, the banks; *i i*, warm-

Fig. 407.



ing and cooling ovens; *h h*, tempering ovens; *e e*, the breast-walls; *f f*, the splint walls; *l l* are small hearths to increase the heat in the tempering-oven when repaired. In Fig. 407 *l* is the flue; *y y* are blocks of stone bearing the wooden frame-work, *z z*, on which the wood used as fuel is placed to dry. Fig. 408 shows the bank, *f f*, on which the melting-pots, *h h h*, stand; over these pots are the work-

Fig. 408



holes; *n n* are the side chambers. In Fig. 409, *b b* is the key-stone; *c d* are the banks; *g* the flue, although in most glass-ovens there are no flues. The flame from the fuel burning in both grates, *m m*, Fig. 408, after heating the melting-oven, passes by the tempering-rooms, and finally to the chimney-stalk.

Siemens' gas-oven has lately found extensive use. At the Paris International Exhibition of 1867 this oven obtained the gold medal. It consists of two parts, the generator, Fig. 410, and the melting-oven, Fig. 411. These parts are separate, and can be 30 or more metres from each other, being connected by a large gas-pipe. The fuel, brown coal, turf, stone coal, or wood, is placed in a generator at *A*, Fig. 410, and falls on the sloping grid, *O*. The gas, a mixture of carbonic oxide and nitrogen, ascends at a temperature of 150° to 200°, and flows out of the generator by a large

pipe, *V*, 4 to 5 metres in height, and is conveyed thence by a horizontal pipe to the melting-oven. The upper chambers of the melting-oven are similar to those of the usual ovens. *P P* are the melting-pots. The gas first passes into the first system of regenerators, the stones of which are raised to a red heat, and passes thence to the melting-room, where it meets with air heated in like manner. The products of combustion then pass to the second regenerating system, the stones of which are cold until heated by the passing gases. The waste gas is finally conducted to the chimney-stalk. When stone-coal is used in the generator, lead-glass may be melted in the oven in open vessels without reduction. The saving of fuel in comparison with the old system is about 30 to 50 per cent.

Fig. 409.

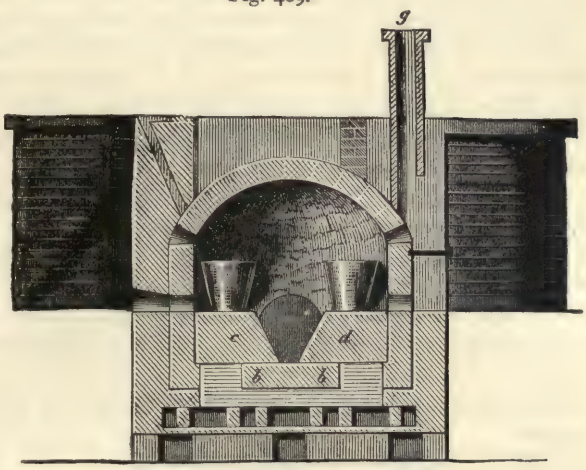
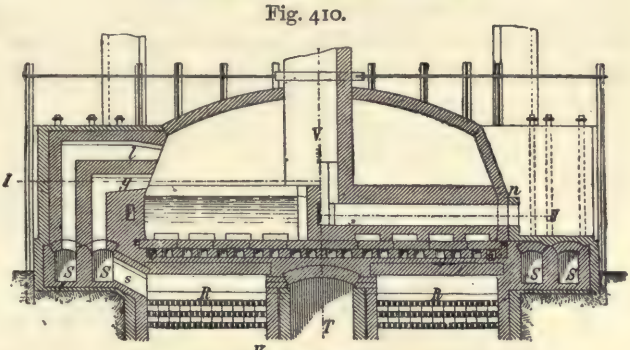


Fig. 410.



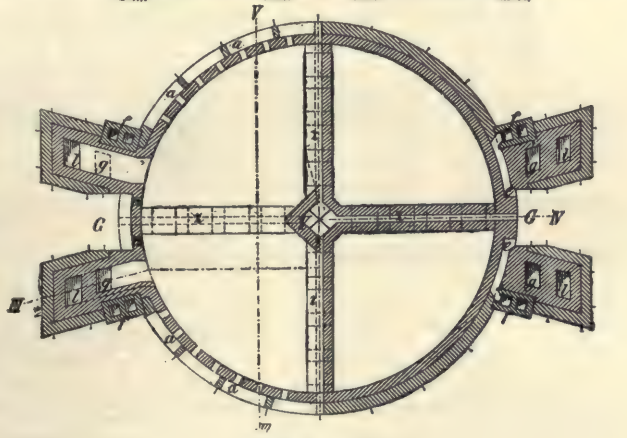


Fig. 411.
Section I.–II.

For manufacturing bottles, &c., on the large scale, the continuous glass-melting tank of Siemens (Figs. 74 to 76, pp. 67, 68) has proved satisfactory. The mixture, as it is introduced at *c*, sinks to the bottom as it melts, and thereby drives upwards another portion of glass, which has become stiffer by cooling at the bottom and in consequence specifically lighter. This portion, again, after being exposed for a time to the heat of the surface and thoroughly fused, becomes specifically heavier than the subjacent masses, and must consequently descend. This behaviour of the glass, determined by the differences in specific gravity, in conjunction with the hydrostatic pressure exerted by the glass-makers standing on the stage, *M*, occasions an undulatory movement of the glass towards the work-places in the direction of the arrows. This ascending and descending movement and continuous progress cause the glass to be thoroughly

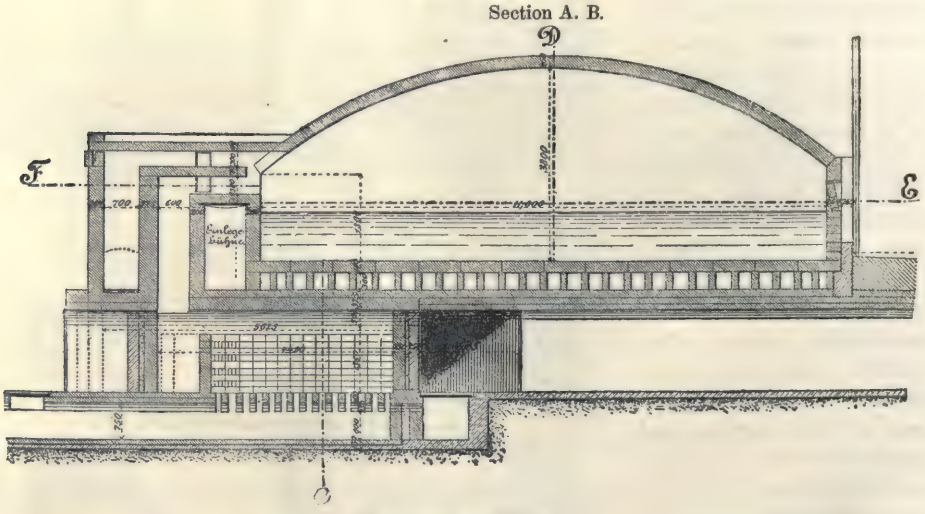
melted through, so that the particles of glass are thoroughly purified if they come to be worked. As the floating fenders dip rather deep into the mass, the glass must sink almost to the bottom, and consequently devitrification is avoided. The generator-gases and the air issue separately through the channels, *g* and *l*, the flame strikes across through the furnace, the products of combustion escape through the opposite channels to the heat accumulators, *R*, and arrive in the chimney through the channels, *x*. By this arrangement of the channels, *g* and *l*, the glass in the free space of the tank before the fenders receives the greatest heat.

The tank-furnaces, Figs. 410 and 411, which F. Siemens uses in the glass-works at Neusattel-Ellbogen, approximate to the ordinary glass-furnace for melting-pots, as it can be used for the most different kinds of glass. The tank is divided into four compartments by bridges placed crossways. The raw materials, introduced separately, are mixed at *G*, and from here passed into the furnace through the apertures, *n*. The regenerators, *R*, forming the base of the furnace, 2 metres broad and 2·75 long (between which is the access-vault, *T*), are connected by the channels, *s*, with the lateral channels, *S*, from which gas and air arrive into the furnace through the channels, *g* and *l*. The round tank is divided into four compartments for four different kinds of glass, by the bridges, *z*, which intersect each other at right angles.

The refrigerations of these bridges run into the common ventilating chimney, *V*, which is carried through the vault of the furnace. Its lower part is divided by an iron cross, about 1 metre high, in such a manner that the ventilation of each bridge is kept apart from the others to above the level of the glass. This is to prevent mutual

Fig. 412.

Section A. B.



Explanation of Term.

Einlegebühne Introductory Stage.

disturbance in the aëration of the several bridges. The bottom and the side walls of the tank are provided with air-refrigerators, *e*, which open into the four small chimneys, *f*, in such a manner that, in case of accident, one compartment may not affect the others. The air-channels of the bridges are separated by large stones of corresponding shape, which rest upon a number of small pillars.

Before each of the 28 work-places, *a*, there floats in the half-melted mass a refining-boat, which renders continuous working possible. Every working place is occupied by

a workman and an assistant, so that the work is carried on in twenty working hours daily in two 12-hour shifts. Each work-place produces hourly 50 bottles.

Latterly, F. Siemens proceeds on the supposition that large spaces are necessary for producing a great heat. Hence he has built a tank-furnace which, as shown in Figs. 412–414, has a very lofty vault.

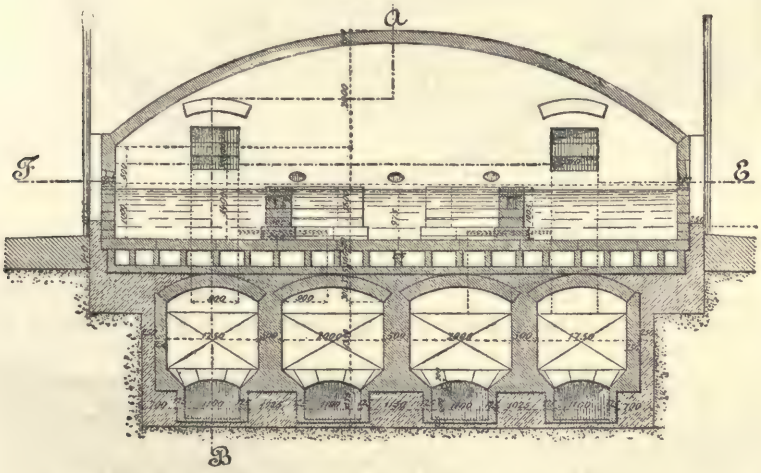
The furnace of Boetius is most widely used in Germany next to that of Siemens.

Glass-melting.—At the temperature of a glass furnace, 1200° to 1250°, the melted glass is a thin liquid, like a thick solution of sugar. This condition is very important for the purification of the glass, since all substances which cannot dissolve in the mass separate out, either on the surface or at the bottom. In this state, further, glass can be cast. At a red heat glass becomes very extensible and flexible, conditions on which the mechanical treatment of glass depends. Two pieces of red-hot glass can be made to unite by being simply pressed together. In spinning glass the material is brought to its utmost degree of extensibility, so that it can be manipulated upon a wheel. The glass thread of Brunfaut's, at Vienna, which is now used for producing wadding, feathers, veils, nets, &c., has, according to the measurements of Fr. Kick, a diameter of 0·006 to 0·012 millimetre. It is, therefore, rather finer than the single cocoon thread.

Not until the furnace has reached its highest temperature is the cullet and then the mixture put into the crucibles, an operation performed in three or four lots.

Fig. 413.

Section C. D.



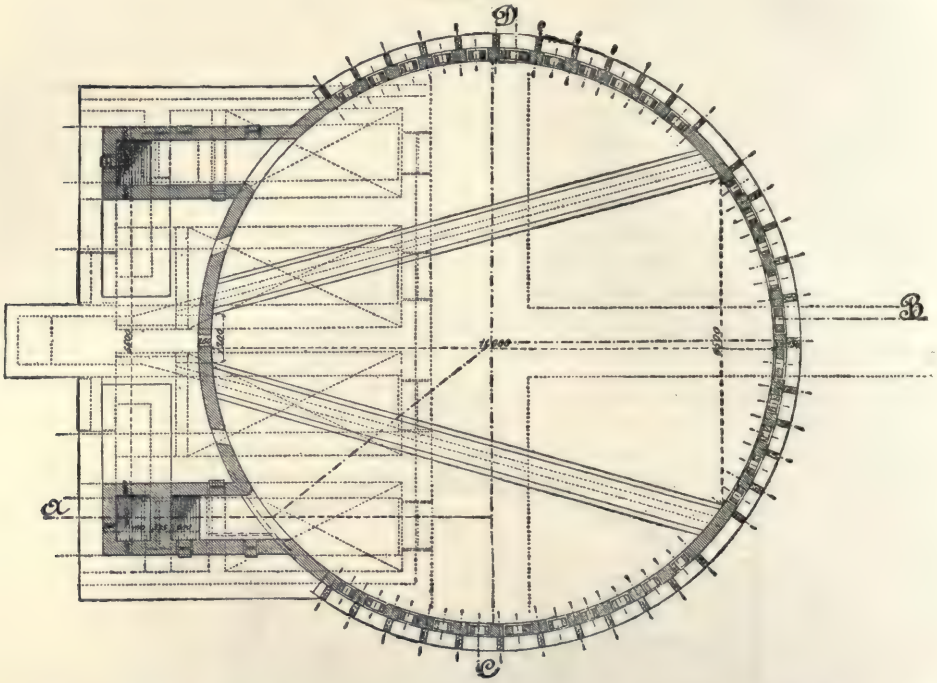
Melting the Glass Material.—When the temperature of the melting-oven has reached the required degree, the material first frits together and is then melted. The oven must be heated equably throughout. At the melting-point the siliceous earth combines with the potash, soda, lime, alumina, lead oxide, &c., to form glass. The substances not taken up form a scum, known as glass-gall, upon the molten glass, which is removed by the aid of iron shovels. This scum is generally composed of sodium sulphate and chlorides of the alkalies. The progress of the melting process is from time to time ascertained by removing a sample of the glass by the help of an iron rod terminating in a flat disc—in fact, a large flat spoon.

Clear-melting.—When the mass is well molten it is "cleared"—that is, maintained for some time at such a temperature that the glass remains in a thinly fluid condition. During this period the uncombined substances settle to the bottom of the melting vessel, the air-bubbles disappear, and the glass-gall still remaining is volatilised or separated. At the commencement of the melting the disengagement of the gases from the molten

mass causes an advantageous agitation, by which the several constituents of unequal specific weight and different composition become well mixed. After the disengagement of the gases the lower part of the melting vessel is at a lower temperature than the upper part; consequently the molten glass is well stirred with the iron ladles or

Fig. 414.

Section E. F.



"poles." Lastly, a piece of either arsenious acid, damp wood, raw turnip, or any other water-containing substance, is introduced to the bottom of the vessel on an iron rod, the end in view being the violent agitation of the molten glass by the steam evolved.

If the mixture consists of soda, calcium carbonate and silica, the process is—

$$Na_2CO_3 + CaCO_3 + 2SiO_2 = Na_2Ca(SiO_3)_2 + 2CO_2.$$

But if salt-cake is employed—

$$2Na_2SO_4 + C + 2SiO_2 = 2Na_2SiO_3 + CO_2 + 2SO_2.$$

In the course of melting the sodium silicate is transformed with the calcium carbonate and the silica as follows:—$Na_2SiO_3 + CaCO_3 + SiO_2 = Na_2Ca(SiO_3)_2 + CO_2$.

Cold-stoking.—After the completion of the clearing follows the cold-stoking—that is, the lowering the temperature of the oven till the glass attains a tough fluid consistency requisite before it can be blown. The glass remains at this temperature, 700° to 800° C., during the rest of the manufacture.

The length of the several processes is as follows:—

Melting	10 to 12 hours.
Clearing	4 to 6 ,,
Blowing	10 to 12 ,,

so that five to six meltings can be effected in a week.

Defects in Glass.—It is extremely difficult to prepare glass perfectly free from blemish. The principal defects are—streaking, threading, running unequally, or

dropping, stoning, blistering, and knotting. Streaking follows from heating the glass unequally, another consequence of which is the threading or the formation of the striæ, by glazing, into coloured threads, generally green. By dropping is understood the lumps or globules formed in the glass by the glazing of the clay cover of the melting vessel, and its combination with the volatilised alkalies, the crude glass thus formed on the cover dropping into the molten glass contained in the vessel. Blistering is a common result of the imperfect clearing of the glass from air bubbles. Lastly, knotting, another common defect, results from uncombined grains of sand taken up in the glass; the small particles of the oven and melting vessel detached during the melting similarly giving rise to stoning. Other defects, such as the imperfect combination of the materials, arising from carelessness or inability of the workman, need not here be noticed.

Various Kinds of Glass.—Glass is divided according to its composition or method of manufacture into —

I. *Glass free from Lead.*

A. Plate glass.
 a. Window glass :—
 α. Rolled glass.
 β. Crown glass.
 b. Plate glass :—
 α. Blown plate glass.
 β. Cast plate glass.

B. Bottle glass.
 a. Ordinary bottle glass.
 b. Medicine and perfumery glass.
 c. Glass for goblets, drinking glasses. &c.
 d. Water pipes and gas tubes.
 e. Retort glass.

C. Pressed or stamped glass.

D. Water glass.

II. *Glass containing Lead (Flint Glass).*

A. Crystal glass.
B. Glass for optical purposes.
C. Enamel.
D. Strass.

III. *Coloured and Stained Glass.*

Plate and Window Glass.—Glass melted in muffles or vessels is manufactured as plate glass or as crown glass. Plate glass, as its name implies, is formed in large or small plates; window glass is generally either ordinary bottle glass or a finer glass of a whiter colour. Recently, thick has taken the place of thin glass for windows, but the colour is hereby considerably increased. That window glass should be prepared cheaply is an essential point; consequently crude materials are employed—crude potash and soda, wood ash, salt cake, ordinary sand, and broken glass from the warehouses, &c. Plate or window glass is generally composed of 100 parts sand, 30 to 40 parts crude calcined soda, 30 to 40 parts calcium carbonate. Instead of the soda may be substituted an equivalent quantity of salt cake. Benrath (1869) found in several kinds of plate glass the following constituents :—

Silicic acid . . .	70·71	...	71·56	...	73·11
Soda	13·35	...	12·97	...	13·00
Lime	13·58	...	13·27	...	13·24
Alumina and ferric oxide . .	1·92	...	1·29	...	0·83
	99·56	...	99·09	...	100·18

Tools.—The tools ordinarily used by the glassblower in the preparation of plate and crown glass are the following :—

The pipe or blow-tube, Fig. 415, is an iron pipe 1·5 to 1·8 metre in length, 3 to 5 centimetres thick, and 1 centimetre interior diameter. *a* is the mouth-piece, made

Fig. 415.



Fig. 416.



Fig. 417.

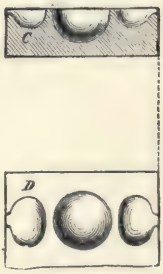


Fig. 418.



Fig. 419.



so as to turn easily between the lips. *c* is a hollow handle from 0·3 to 0·5 metre in length. *b* is the part attached to the glass.

The handle or hand irons are rods 1 to 1·3 metre in length, used to transport the hot vessels, &c. The marbel, Figs. 416 and 417, is a piece of wood with semi-globular indentations, which serve as matrices for the glass to be taken up on the blower's pipe. The whip, Fig. 418, is a block of wood, hollowed so as to form a long neck to the soft semi-molten glass; it is also used to remove the glass from the pipe. Fig. 419 is the shears used for trimming the molten glass, and to cut openings during the blowing of various articles.

Window glass is manufactured as crown glass or as rolled glass.

Crown Glass.—Crown glass is the oldest kind of window glass. It is formed in the manufacture as a disc of glass, generally of about 6 inches in radius from the periphery to the centre knot left by the glassblower's pipe, technically termed the bull's-eye. The largest discs are scarcely 64 to 66 inches, from which a square plate of 22 inches only can be cut, the bull's-eye interfering with the cutting of a larger size. In the preparation of this glass three workmen are employed; the first takes so much molten glass on the end of a pipe as will serve for a single disc, and passes pipe and glass to the second workman, the blower. He blows the glass into a large globe or ball, which, when finished, he hands to a third workman, the finisher, who opens the globe and forms the sheet or pane. The labour is divided in detail in the following manner :—The first workman receives the warm pipe, thrusts it into the vessel of molten glass, and turns it steadily round until he has collected upon the end a knob of glass of sufficient size. The weight of this knob is generally 10 to 14 lbs. The first workman by means of the marbel imparts somewhat of a spherical form to the solid glass ball, which is now taken in hand by the blower, who by turning and shifting the glass about, at the same time blowing through the tube, perfects the hollow spheroid. The glass has by this time cooled considerably, and with the pipe is therefore returned to the oven, the tube of the pipe being fastened in a fork or hook in the ceiling of the oven. As the globe of glass is gradually heated the weight of the rod causes it to flatten out, and it is removed by the finisher as a disc of nearly molten glass. He places the tube in the cavity of the whip, and by a series of dexterous movements perfects the shape, enlarges the disc if required, or in some cases makes a larger disc by removing the partially

flattened sphere from the oven, opening the bottom with a maul or iron rod, and causing the glass to take the form of a disc by means of the centrifugal force resulting from a rapid rotary motion of the rod. Finally, the discs are separated from the pipe by the help of a drop of cold water, and are next placed in an annealing oven, to the number of 150 to 200, to cool. The finished plates are cut to the required size; the centres or bull's-eyes serve for the making of strass and for other purposes.

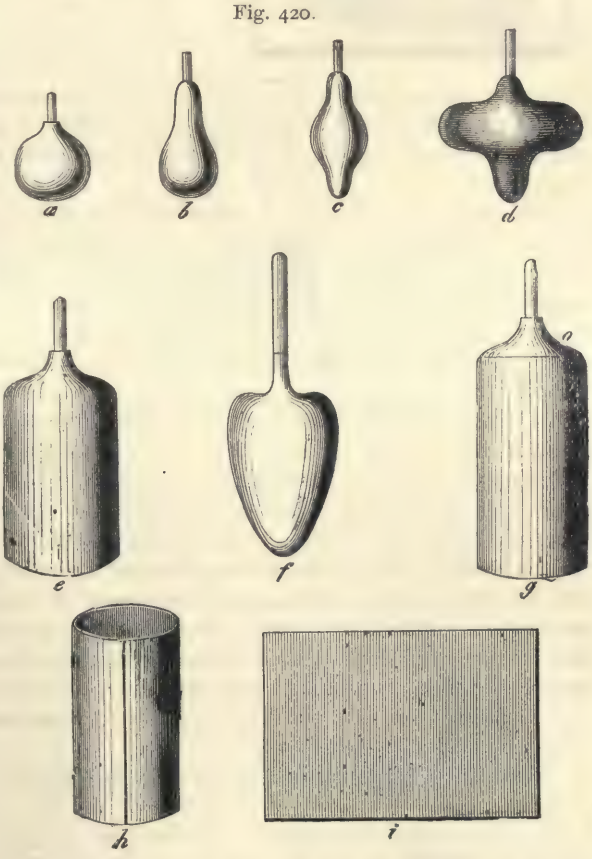
Sheet Glass, or Cylinder Glass.—Rolled or sheet glass is made by cutting a glass cylinder or roll throughout its length, and beating or rolling it out flat on a table. It is for this reason termed sheet glass. Usually this sheet glass is used for ground glass, and is further separated into ordinary sheet or roll glass and fine sheet glass, the latter having larger dimensions.

The preparation of sheet glass is one of the most difficult processes of glass manufacture; it may be considered as consisting of two operations—

1. The blowing of the roll, or cylinder; and
2. The flattening.

After the molten glass has cleared, and attained the barely fluid consistency before mentioned, the workman inserts his pipe into the mass, and by turning manages to accumulate on it a globe of glass, during the time blowing into the tube to keep it clear of the molten glass. The glass now takes the form *a*, Fig. 420. By continued manipulation in the marbel, and by blowing, the enlarged forms, *b* and *c*, and finally *d*, are obtained. The glass has by this time cooled, and is taken to the oven to be re-heated. When this is effected, the workman, by means of his tools, by a continued rotation of glass, and by blowing, brings the globe to the shape represented by *f*. He then opens out the bottom of this form with a maul-stick, and obtains the cylinder *e*, which is separated from the pipe by dropping a little cold water upon the neck, *o*, joining the two. The removal of this neck is next effected by means of a red-hot iron rod, which also serves to open the cylinder throughout its length as shown by *h*.

Fig. 420.



After a great number of these cylinders have been blown, the operation being generally continued for three days, the opening into plates is commenced. The cylinders are placed in an oven termed the plate-oven, shown in ground plan in Fig. 421, consisting of two chambers, one the heating room, C, and the other the tempering or

annealing room, D. In the passage B, the heated glass rolls or cylinders, *a a a*, are suspended upon two iron rods, where they are maintained at a certain heat. The most important part of the plate-oven is the platten, C, made of a well-rammed fire-clay. A similar plate, D, is placed in the annealing room. When sufficiently heated, the cylinders are brought to the flattening table, *c*, Fig. 422, where they are speedily opened

Fig. 421.

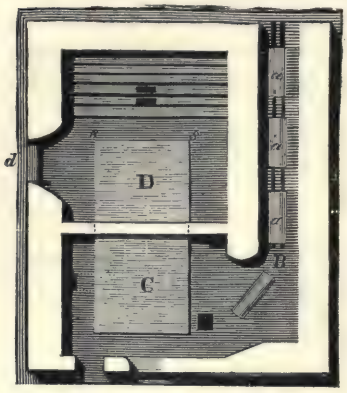
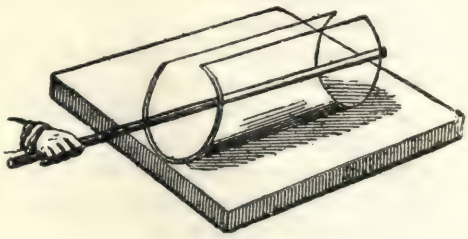


Fig. 422.



out in the manner shown in the woodcut. A workman stationed at *d*, Fig. 421, receives the flat panes of glass, and leans them against the iron bars, *s s*, in the annealing room, whence, having gradually cooled during four or five days, they are removed to be sorted and packed.

Plate Glass.—Plate glass is either blown or cast. The manufacture is very similar to that of table glass just described. The materials are in great part the same as those employed in the manufacture of fine white glass. This branch of glass manufacture is most strikingly illustrative of the rapid growth of the industry during the last ten or twenty years. Formerly plate glass was esteemed an article of luxury, whereas now it is that most generally used for workshop windows, carriages, showrooms, &c., and for windows of private residences. It far surpasses in transparency and elegance the small panes formerly used. By the Glass Jury of the International Exhibition of Paris of 1867, it was surmised that before ten years had elapsed plate glass would be that most generally in the market. The blowing of plate glass is effected with the same tools as the blowing of table glass; and the cylinder is obtained in a similar manner. The lump of glass taken by the blower on his pipe from the melting vessel weighs about 45 lbs., from which a plate of 1·5 metre in length and 1 to 1·1 metre breadth by 1 to 1·1 centimetre thickness is obtained. But the chief method of making plate glass is by casting. Cast plate glass is always made from pure materials, and may be considered as a sodium-calcium glass free from lead. Potassium-calcium glass is far more expensive, being almost a colourless glass. In England, Belgium, and Germany the raw materials used in manufacturing cast plate glass are—sand, limestone, and soda, or salt cake.

Benrath (1869) found in English (*a*) and in German (*β*) plate glass:—

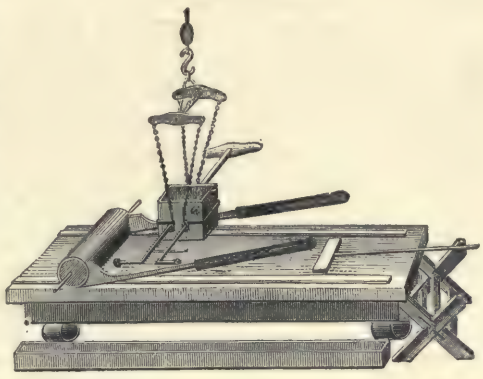
	a.		*β.*
Silica	76·300	...	78·750
Soda	16·550	...	13·000
Lime	6·500	...	6·500
Alumina and oxide of iron	0·650	...	1·750
	100·000	...	100·000
Sp. gr.	2·448	...	2·456

The following description of casting the plates is mainly founded upon the method pursued at St. Gobain and Ravenhead. The manufacture is included in—

1. The melting and clearing.
2. The casting and cooling.
3. The polishing; including—
 - *a.* The rough polishing.
 - *β.* The fine polishing.
 - *γ.* Finishing.

The Melting and Clearing.—The melting and clearing vessels are of very different form and size. The first is a conical vessel surmounted by a cupola having three apertures, making an angle of 120° with each other. The clearing pans are small, wide, and low vessels. These vessels are never in the same oven. After the materials are melted, which is effected in sixteen to eighteen hours, the molten mass is poured into the clearing vessels. The impurities are then removed with a large copper ladle, this process occupying about six hours. During the clearing the excess of soda is volatilised. When the glass is sufficiently cleared the casting commences. The vessel containing the molten glass is taken up by a crane and swung to the casting table, this table or mould being on a level with the cooling or annealing oven. The casting table consists of a large polished metal plate, Fig. 423, in the French works of copper or bronze, 4 metres long, 2·25 metres wide, and 11 to 18 centimetres thick. The plate at St. Gobain weighs 55,000 lbs. and cost 100,000 francs (£4000). In England the plates are of cast-iron, 25 centimetres thick, 5 metres in length, and 2·8 metres wide. In order that the glass plate shall be of equal thickness, a bronze or cast-iron roller passes over the surface on guides of the thickness required. The metal plate is first warmed to prevent the sudden cooling of the glass. The operation of casting includes—

Fig. 423.



- *a.* The conveyance of the pan to the table.
- *b.* The cleansing of the plate and the pan.
- *c.* The casting and conveyance of the plate to the annealing room.

The cooling room has two fire-places and three glass tables. The temperature is at first that of the glass plate introduced. So soon as three plates are placed in the oven, all the openings are closed, and the glass left for a day to cool. The cooled glass plate is taken out of the annealing oven to the cutting room, laid on a cloth-covered table, and cut to size with a diamond.

Polishing.—The glass plate is cut into tablets. The under side of the plate, where it has been in contact with the table, is smooth, while the upper surface is wavy, and requires to be polished. This is effected by fastening the plate or tablet to a bench with plaster-of-Paris, and grinding the upper surface smooth with some sharp powder; or another plate is caused by machinery to move above the former in such a manner that the surfaces of both are ground smooth. The ground plates are then removed to the polishing table, where a similar process is gone through, but with a finer powder. Finally, when placed upon the finishing table, only the finest powder and leathern pads are employed. By grinding and polishing, the glass sometimes loses half

its weight in thickness. Suppose a plate-glass manufactory to produce 400,000 square feet of glass annually, there will be with this amount of glass, weighing about 16,000 cwts., a loss of 8000 cwts., corresponding to 2700 cwts. of calcined soda, and a money value of more than £1000.

Silvering.—After polishing, each glass tablet intended to make a looking-glass is silvered, or, more correctly, coated on one side with an amalgam of tin. In the preparation of this amalgam tinfoil is used, but it must be beaten from the finest tin, and possess a surface similar to that of polished silver. The art of silvering is simple, and merely requires dexterity. The glass plate having been thoroughly cleansed from all grease and dirt with putty powder and wood ash, the workman proceeds to lay a sheet of tinfoil smoothly upon the table, carefully pressing out with a cloth dabber all wrinkles and places likely to form air bubbles. He spreads over it a quantity of mercury, taking care that all parts are equally covered, and then the glass plate is pushed gently on to the surface, commencing at one edge. A glass plate of 30 to 40 square feet requires 150 to 200 lbs. of mercury, although the amalgam is not so thick as a sheet of the finest paper. The glass is allowed to remain for twenty-four hours. It is then removed to a wooden incline similar to a reading desk to allow of the excess of mercury draining off. As the amalgam gradually sets, the incline is increased till finally the plate reaches the perpendicular, when the process is finished, and the mirror removed to the store room.

Silvering by Precipitation.—The former method of coating the glass with tin-amalgam obtains its name of silvering by analogy only: the true process of silvering is the following, patented in 1844 by Mr. Drayton:—32 grammes of silver nitrate are dissolved in 64 grammes of water and 16 grammes of liquid ammonia, adding to the filtered solution 108 grammes of spirits of wine of 0·842 sp. gr., and 20 to 30 drops of oil of cassia. Call this fluid No. 1. Another fluid (No. 2) is prepared by mixing 1 volume of oil of cloves with 3 volumes of spirits of wine. The workman places the glass plate upon a table, carefully levels it, and floods it to a depth of 0·5 to 1 centimetre with fluid No. 1. He then precipitates the silver by adding 6 to 12 drops at a time of fluid No. 2 until the whole of the surface is covered. For every square foot of glass 9 decigrammes of silver nitrate are required. Liebig recommends an ammoniacal solution of fused silver nitrate to which 450 c.c. of soda-lye of 1·035 sp. gr. are added. The precipitate thrown down is dissolved by means of ammonia, the volume being increased to 1450 c.c., and by water to 1500 c.c. This fluid is mixed shortly before application with one-sixth to one-eighth of its volume of solution of sugar of milk, containing 10 parts by weight to 1 of sugar of milk. The glass is flooded with this fluid to about half an inch in depth; reduction soon sets in, and the glass becomes thickly coated. 1 square metre of glass plate requires 2·210 grammes of silver. The plate is then dried, cleaned, and polished. Lowe employs silver nitrate, starch-sugar, and potash; A. Martin, silver nitrate, ammonia, and tartaric acid.

Platinising.—According to the researches of Dodé, platinum may be used for coating plate-glass. In France, Creswell and Tavernier have already brought platinised mirrors before the public. Hitherto platinum had been used in ornamenting porcelain, and the glass plates are prepared in a similar manner, the metal being burnt in, as it is termed. The platinum is precipitated from its chloride by oil of lavender, the chloride being spread equally over the glass with a fine-haired paint-brush. The plate is then placed in a muffle. Cheapness is a prominent feature of this process; as by it all faulty glasses can be very easily repaired, those by the old methods being thrown aside as useless. In Paris the lids of boxes and fancy articles are largely manufactured from platinised glass.

For gilding glass there is employed a dilute solution of sodium aurate, which is reduced by means of a saturated solution of ethylene in alcohol.

Bottle Glass.—Bottle glass includes all kinds of glass made into vessels for holding fluids. It is made from common green glass, from fine white glass, and from crystal glass. Medicine bottles, &c., are made from common green glass; tumblers, or drinking glasses, from fine white glass; and crystal glass is employed for the same articles, but selling at a higher price.

The materials for ordinary bottle glass are sand, potash or soda, basalt, &c. For medicine glass the materials must be free from iron, and still purer for articles of white glass. In the manufacture of bottle glass no considerable amount of care is required, the desiderata being strength and sufficient resistance to the action of ordinary acids. The processes of melting and annealing are conducted in the ordinary manner. The analyses of several glasses gave the following results:—

Silicic acid	74·71	74·66	75·94	74·37	74·26			
Potash	—	4·32	—	12·48	—			
Soda	15·74	11·01	15·15	3·42	14·06			
Lime	8·77	9·13	8·01	9·02	8·60			
Alumina	0·43				2·52			
Iron oxide	0·14	0·88	0·90	0·71	0·38			
Manganese oxide	0·21				0·18			
	100·00	100·00	100·00	100·00	100·00			
Sp. gr.	2·47	2·48	2·47	2·30	2·40			

The details of the several processes of bottle glass manufacture are, after the making of the rough shape out of the tough fluid glass, so various that only single examples can be given. We will select the ordinary wine bottle. The glass blower, taking some molten glass on his pipe, turns and moulds it into the shape of *a*, Fig. 424. By continued blowing the enlarged form, *b*, is obtained; this form, still more enlarged, as at *c*, is placed in the mould, *d*. The workman now blows sharply into the incipient bottle, the glass filling out the mould and producing the sharp curve of the shoulder of the wine bottle. The rod or puntili, *e*, is now introduced, and a firm footing given by pressing in the bottom of the bottle. While the blower prepares a new bottle, the assistant places that already formed in the annealing oven. In the making of flasks

Fig. 424.

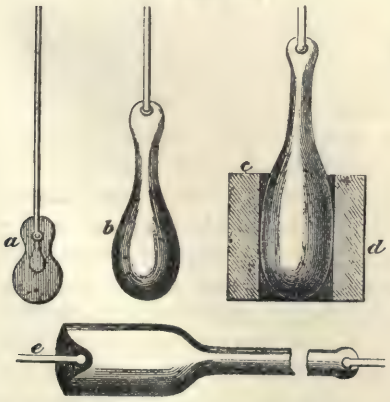
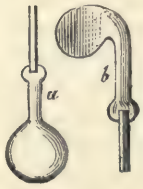


Fig. 425.



Fig. 426.



and retorts the flask tongs, Fig. 425, are employed, the neck being allowed to remain straight, as at *a*, Fig. 426, to form a flask, or bent, as at *b*, to make a retort. The manufacture of a beaker will be readily understood from Figs. 427 and 428, *A*, *B*, *C*, being the method of producing a globular body, and *a*, *b*, *c*, a beaker with nearly perpendicular sides. Glass-tubing is drawn out as shown at Fig. 429. Glass rods are similarly made, but without blowing.

Pressed and Cast Glass.—Pressed or cast glass comprises the many cheap glass ornaments, and indeed, ornamental glass-work of all kinds, now so general. The tall, narrow-mouthed chimney ornaments are thus made by being blown into engraved brass moulds, instead of into plain moulds as in the case of the bottle. Cup-shaped articles

Fig. 428.

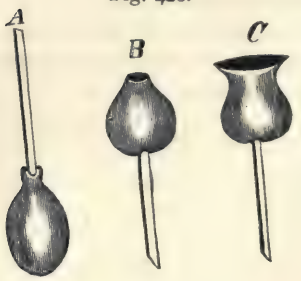


Fig. 428.

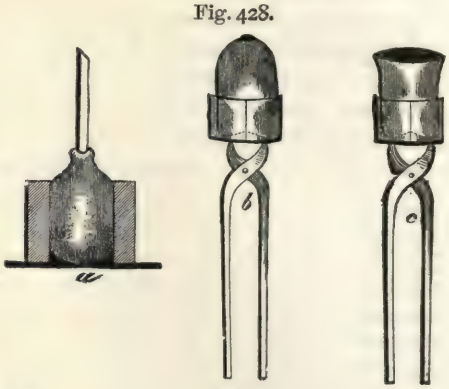


Fig. 429.



are made with molten glass pressed between a concave and convex surface, the surplus glass escaping at some point purposely arranged. As a rule, the objects taken from the moulds require but little polishing.

Hardened Glass.—The invention of hardened glass by De la Bastie (1875) excited a greater sensation than do most novelties, but the sanguine hopes entertained of its usefulness have not been fulfilled. The process consists essentially in a rapid, uniform cooling of the glass when in a soft state after it has been already blown or otherwise shaped. By this means it acquires such a physical character that it withstands blows or other external attacks better than ordinary glass which has been cooled slowly in the usual manner. Besides the oil-baths used by De la Bastie must be noticed the process of hardening with cold, solid objects, *e.g.*, plates of clay, proposed by Fr. Siemens.

The glasses to be hardened, after they have been heated to softness, are subjected to a sudden chill, which may be effected by very various means. In consequence of the rapid cessation of the state of softness there sets in a state of molecular tension to which the hardened glass is indebted for its peculiar properties. The glass to be hardened must be well melted and clarified, and should contain neither unmelted quartz grains nor glass gall. Articles of badly clarified, streaky glass generally burst in the hardening bath. The external form and the thickness of the vessels have a great influence upon the results. Vessels with thick sides have to be hardened in very thick baths, and the chilling must not be too sudden. The temperature which must be given to the objects is that at which the glass softens, and they are plunged into the bath either directly after being blown or after being re-heated. At the first introduction of the process it was supposed that the chemical composition of the hardening bath was a point of importance, only certain oils and fats being suitable and elementary substances being excluded. It was soon found that the physical properties only of the hardening baths were of importance. One and the same quality of glass can be tempered equally well in different baths, but the temperature must be higher or lower according to their conductivity. Baths which conduct heat well require a higher temperature than those which have a low conductive power, if the chilling effect is to be alike in both. The first group of substances selected for tempering baths comprise liquids and solids which are liquefied at the required temperature, *e.g.*,

mixtures of fats, oils, glycerine, paraffine, hydrocarbons, saline solutions, and easily fusible alloys. Pure water is excluded. Glasses which have been hardened in an oil bath at 70° burst if plunged into water of the same temperature. Baths composed of fats have proved most satisfactory, the better, in general, the longer they have been in use.

The objections to fat baths are their costliness, their combustibility and the fact that their temperature is continually raised by the introduction of hot objects.

In the case of solid bodies the hardening is effected simultaneously with shaping. In liquid baths the softened objects, especially plates, lose their shape more or less. For the goodness of hard glass it is important that both the heating and the chilling are effected with the utmost possible rapidity. It is also important that the glass should be heated to the highest point at which it can be lifted out of the furnace.

A hardened glass plate of 16 centimetres in length, 12 centimetres in breadth, and 5 millimetres in thickness bore the fall of a weight of 200 grammes from the height of 4 metres. A similar plate of common glass was broken by a weight of 100 grammes falling a height of 30 to 40 centimetres. Hardened glass also bears pressure to about four times the extent of common glass. But the same tension which gives to hardened glass its elasticity and solidity is the cause of explosive disruptions if suddenly liberated at any one point. Articles which are exposed to shocks or blows on their sides or corners should not be hardened—*e.g.*, plates, beakers, capsules, &c. A hardened glass plate which bears the fall of considerable weights if struck in the middle breaks easily by a blow on its edges, especially from a narrow instrument. In common glass only a few splinters may be broken off, so that the vessel may still be fit for use, whilst hardened glass is completely shattered. Hence the process cannot be recommended for bottles, drinking glasses, &c.: whilst window panes or plates, which are mostly exposed to blows on the surface, where they are most resistant, are much better fitted for hardening. The great objection to hardened glass is that there is no means of distinguishing good from bad articles until they come into actual use. Hence the original confidence of the public has been succeeded by justifiable distrust. For laboratory apparatus hardened glass is quite unfit, and for domestic purposes it is at least very doubtful. Hence it has almost entirely disappeared from commerce.

Soluble Glass, Water Glass.—By water glass is understood a soluble alkaline silicate. Its preparation is effected by melting sand with much alkali, the result being a fluid substance, first observed by Van Helmont in 1640.

It was made by Glauber in 1648 from potash and silica, and by him termed fluid silica. Von Fuchs, in 1825, obtained what is now known as water glass by treating silicic acid with an alkali, the result being soluble in water, but not affected by atmospheric changes.

The various kinds of water glass are known as—

Potash water glass.
Soda ,,
Double ,,
Fixing ,,

Potash water glass is obtained by the melting together of pulverised quartz or purified quartz sand 45 parts, potash 30 parts, powdered wood charcoal 3 parts, the molten mass being dissolved by means of boiling in water. The solution contains much potassium sulphide, which is removed by boiling with copper oxide. The addition of carbon assists in reducing part of the carbonic acid to carbonic oxide, which disappears during the melting. Soda water glass is prepared with pulverised quartz 5 parts, calcined soda 23 parts, carbon 3 parts; or, according to Buchner, with pulverised quartz 100 parts, calcined Glauber's salts 60 parts, and carbon 15 to 20 parts. Double water glass (potash and soda water glass) is prepared, according to Doebereiner, by melting together quartz powder 152 parts, calcined soda 54 parts,

potash 70 parts; according to Von Fuchs, from pulverised quartz 100 parts, purified potash 28 parts, calcined soda 22 parts, powdered wood charcoal 6 parts. It is further obtained by melting potassium and sodium tartrate,

$$\left.\begin{matrix}\mathrm{Na}\\ \mathrm{K}\end{matrix}\right\}\mathrm{C_4H_4O_6} + 4\mathrm{H_2O},$$

with quartz; from equal molecules of potassium and sodium nitrate and quartz; from purified tartar and sodium nitrate and quartz. It is more fusible than the foregoing. For technical purposes a mixture of—

3 volumes of concentrated potash water glass solution,
2 „ „ soda „ „

is employed. By the name of fixing water glass, Von Fuchs designates a mixture of silica well saturated with potash water glass and a sodium silicate, obtained by melting together 3 parts of calcined soda with 2 parts of pulverised quartz. It is used to fix or render the colours permanent in stereochromy.

The kind known commercially as prepared water glass is obtained by boiling the powdered water glass with water; and the solution, as found in the market, is known as of 33° and 66°, the difference being that the first 100 parts by weight contain 33 parts by weight of solid water glass and 67 parts by weight of water. It therefore follows that in solutions of 40° and 66°, the water is proportioned as 60 and 34 parts respectively. Acids, with the exception of carbonic acid, decompose water glass solutions, separating the silica as a gelatinous substance; it should, therefore, be kept in vessels well protected from volatile acids.

Water glass is an important product in industry. It is used to render wood, linen, and paper non-inflammable. The water glass of 33° is first mixed with double its weight of rain-water, and is then treated with some fire-proof colouring matter, as clay, chalk, fluor-spar, felspar, &c. The material to be rendered uninflammable is painted with the solution, and again with another coat after the first has remained twenty-four hours to dry. Wood is thus preserved from being worm-eaten, from incrustation of fungi, &c. Another industrial application of water glass is as a cement; in this it is equal to glue, and, indeed, is known as "mineral glue." Chalk mixed with water glass forms a very compact mass, drying as hard as marble; no chemical change is hereby effected; there is no conversion to calcium silicate or potassium carbonate; the hardening is entirely the result of adhesion. Calcium phosphate treated with water glass acts similarly. Zinc-white and magnesia lose none of their useful properties when mixed with water glass. Another important application of water glass is in the painting of stone and concrete walls, and in the preparation of artificial stone. The latter, first made by Ransome, is daily meeting with more extended application in England, India, and America. It is prepared by mixing sand with sodium silicate to a plastic mass, which is pressed into the required shape, and then placed in a solution of calcium chloride. By this means calcium silicate is formed, and cements the grains of sand together, while the sodium chloride is removed by repeated washings. As cement for stone, glass, and porcelain, water glass is especially useful. It is also employed in the preparation of xyloplastic casts, made of wood rendered pulpy by treatment with hydrochloric acid, and afterwards impregnated with water glass.

Stereochromy.—An interesting and important application of water glass is in the new art of mural and monumental painting, termed by Von Fuchs *Stereochromy* (*στερεος, solid,* and *χρωμα, colour*). In this method of painting the water glass forms the foundation or binding material of the colour. There is first to be considered the mortar or cement ground upon which the painting is to be executed. This ground has to receive an under- and an over-ground. It is essential, of course, that the fundamental groundwork should be of a stone or cement possessing every requisite

for durability. The next, or under-ground, is made with lime-mortar, and is allowed to remain for some time to harden. When well dried, the water glass solution is applied, and allowed to soak well into the interstices of the mortar. After the under-ground has been thus prepared, the over-ground, or that to receive the painting, is laid on. This consists of similar constituents to the under-ground, with the exception that a good sharp sand is used, and the mixture treated with a thin lye of calcium carbonate. This over-ground of fine cement being nicely levelled, and having dried, it is thoroughly impregnated with water glass. When this is dry, the painting is executed in water-colours. Nothing further is necessary than to fix these colours, which is effected by a treatment with a fixing water glass. The colours employed are :—Zinc-white, chrome-green, chrome-oxide, cobalt-green, chrome-red (basic lead chromate), zinc-yellow, iron oxide, cadmium sulphide, ultramarine, ochre, &c. Vermilion is not employed, as it changes colour in fixing, turning to a brown. Cobalt-ultramarine, on the contrary, brightens on the application of the fixing solution, and is, therefore, a very effective colour. As a decorative art stereochromy will doubtless attain great importance, the paintings being unaffected by rain, smoke, or change of temperature.

Crystal Glass.—Crystal glass includes all potash glass containing lead. Crystal glass was first prepared in England. There are a few difficulties in manufacturing this glass. The smoke from an anthracite coal fire is injurious to the pure colour of the glass, so that the melting-pot is provided with a cover; but this addition has the disadvantage that the temperature necessary to melt the glass cannot easily be ascertained. A larger proportion of alkali must therefore be added, which deteriorates the quality of the glass, rendering it liable to after-change. To prevent this as much as possible, lead oxide is used to make the glass more easily fusible, and by this means a beautifully clear, transparent glass results. The following table will give some idea of the proportions of the materials :—

Sand	300
Potash	100
Broken glass	300
Minium	200
Arsenious acid	0·60
Manganese sesquioxide	0·45

The following mixture is used in the glass houses of Edinburgh and Leith :—

Sand	300
Potash	100
Minium	150
Lead-glaze	50

and a small quantity of manganese sesquioxide (braunite) or arsenious acid.

To render the glass fluid, saltpetre is sometimes added, but in moderate quantities. Dumas recommends sand 300, minium 200, dry potash 95 to 100. On the supposition that there is no loss during melting, the mixtures contain :—

Silica	57·4	...	57
Lead oxide	36·3	...	36
Potash	6·3	...	7
	100·0	...	100

The whole melting process is concluded in twelve to sixteen hours. The glass is treated in a manner similar to that already described, but is more easily worked. Benrath (α) and Faraday (β) found crystal glass by analysis to consist of :—

	a.		*β.*
Silicic acid	50·18	...	51·93
Oxide of lead	38·11	...	33·28
Potash	11·61	...	13·67
Alumina, &c.	0·04	...	—
	99·94	...	98·88

According to Benrath, normal crystal glass has the formula $K_{10}Pb_7Si_{36}O_{84}$ (*i.e.*, $5K_2O,7PbO,36SiO_2$).

Polishing.—Crystal glass is either cast in brass moulds or is ground. Its hardness admits of its taking a better polish than other glasses. The grinding wheel is of cast-iron; above the periphery is fixed a vessel containing water and fine washed sand, which constantly drops upon the wheel, assisting in the cutting. The polishing wheel is of wood, well served with pumice-powder and water.

Optical Glass.—The preparation of good optical glass, especially of large dimensions, is a matter of much difficulty. Transparency, hardness, a high refractive power with perfect achromatism are all required, and must be obtained at the outlay of any amount of labour. The glass must also be entirely homogeneous, else the light is not refracted regularly; threads and streaks (striæ) are the results of inequality, and it naturally follows that, if these appear to the unassisted eye, they will seriously affect delicate observations when high magnifying powers are used, as in telescopes and microscopes. It is an error, however, to suppose that these irregularities arise from impurities; they are rather due to interruptions in heating and cooling, or to unequally heating and cooling during manufacture. This must especially be evident in the case of waviness or an undulating structure of the glass. Crown glass, free from lead, is not so liable to faults as flint glass; both these are employed for optical purposes.

The Rev. Mr. Harcourt's experimental researches as to the best optical glass, communicated to the British Association, at the recent meeting at Edinburgh, by Professor Stokes, show fully what has been accomplished in preparing glass of this order. Mr. Harcourt's researches were chiefly carried on with phosphates, combined in many cases with fluorides, and sometimes with tungstates, molybdates, and titanates, owing to the difficult fusibility and pasty consistency of silicate glasses. The experiments included glasses containing potassium, sodium, lithium, barium, strontium, calcium, aluminium, manganese, magnesium, zinc, cadmium, lead, tin, nickel, chromium, lead, thallium, bismuth, antimony, tungsten, molybdenum, titanium, vanadium, phosphorus, fluorine, boron, and sulphur. The molybdic glasses first prepared were of a somewhat deep colour, deteriorating with age; but at length molybdic glass was obtained free from colour, and permanent. Titanic acid gave results much superior to those obtained with molybdic. Glass made with lead terborate agreed in dispersive power with flint glass; while a prism of this glass extends the red and blue ends of the spectrum equally with a prism of one part by volume of flint glass with two of crown glass. Notwithstanding the great difficulties arising from striæ, Mr. Harcourt finally succeeded in preparing discs of lead terborate and of titanic glass, 3 inches in diameter, almost homogeneous.

It is well known that flint and crown glass form an achromatic combination. Flint glass is very easily rendered fluid, conducing to the formation of striæ. A variation of the proportions of the constituent materials, though not producing effects visible to the eye alone, will strongly striate the glass, rendering it unfit for optical purposes. The constituents must be equally distributed throughout, and this is a great difficulty. The oxide of lead, being of so much greater weight, sinks to the bottom, while the lighter constituents float at the upper part of the melting vessel. Usually this is so much the case that glasses of different specific gravities are obtained from the upper and lower parts of the melting-pot.

Bontemps manufactures flint glass in the following manner:—A glass mass is prepared of—

White sand	100 kilos.
Minium	106 „
Potassium carbonate	43 „

and placed over an anthracite or stone-coal fire in a small melting oven shown in Fig. 430 in vertical, and in Fig. 431 in horizontal section. The oven contains only one

Fig. 430.

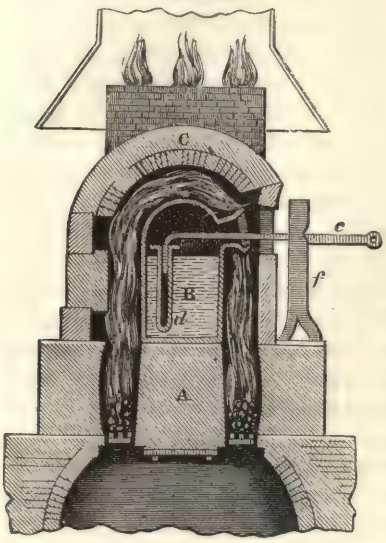
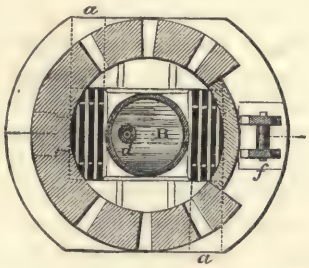


Fig. 431.



covered melting vessel, B, standing on the bank, A *a a* are the grate bars; *c* an iron rake, enclosed in a fire-clay cylinder, *d*, and resting upon the roller, *f*. After about fourteen hours the mass becomes equally fluid; and a red-hot rake is introduced into the vessel, by which the several layers of material are intimately mixed. In about five minutes the mass is sufficiently stirred; the iron rod is then removed, the clay cylinder remaining. This stirring is effected several times without removing the clay cylinder; and the glass is then ready for blowing or casting. But for optical purposes it is, after the removal of the clay cylinder, allowed to cool gradually during eight days in an annealing oven. The most perfect pieces of glass are then cut from the interior of the mass. According to Dumas's analysis of a sample obtained from Guinand, flint glass consists of—

Silica	42·5
Lead oxide	43·5
Lime	0·5
Potash	11·7
Alumina, iron oxide, and manganese protoxide	1·8
	100·0

The second kind of optical glass, crown glass free from lead, contains, according to Bontemps:—Sand, 120; potash, 35; soda, 20; chalk, 15; and arsenious acid, 1 part.

The best optical glass now known is that used by Zeiss of Jena for the object-glasses of his microscopes.

Strass.—The imitation of precious stones is an interesting feature of glass manufacture, and in Egypt and Greece it was an art that attained to great perfection. All precious stones, with the solitary exception of the opal, can be imitated artificially. The chief constituent of these artificial gems is *strass*, or, as it was termed by Fontanier, Mayence base; and in France artificial gems are mostly known as *Pierres de Strass*. This base is colourless, and may be considered as a borosilicate of the alkalies containing lead oxide, this being in larger proportion than in flint glass.

Donault-Wieland found colourless strass by analysis to consist of:—

Silica	38·1
Alumina	1·0
Lead oxide	53·0
Potash	7·9
Borax, Arsenious acid	traces
	100·0

This analysis gives the formula $(3K_2O,6SiO_2) + 3(3PbO,6SiO_2)$.

The various gems are imitated by the addition of colouring oxides, the whole of the materials being ground to a fine powder, intimately mixed, and melted at a strong heat. The imitation of the *topaz* is obtained by taking—strass, 1000; antimony, 40; and Cassius's purple, 1 part. The topaz can also be imitated with—strass, 1000; iron oxide, 1 part. The imitation *ruby* is obtained with 1 part of the topaz paste and 8 parts of strass, the whole being melted together for thirty hours. A ruby of less beauty is obtained with—strass, 1000; manganese dioxide, 5 parts. A good *emerald* can be prepared from—strass, 1000; copper oxide, 8; chromium oxide, 0·2 part. The *sapphire* is obtained from—strass, 1000; pure cobalt oxide, 15 parts. The *amethyst* from —strass, 1000; manganese dioxide, 8; cobalt oxide, 5; Cassius's purple, 0·2. The *beryl* or *aqua marina* is imitated by—strass, 1000; glass of antimony, 7; cobalt oxide, 0·4. The *carbuncle* by—strass, 1000; glass of antimony, 500; purple of Cassius, 4; manganese dioxide, 4 parts. Sufficient attention has not been paid to the mode in which the colouring is effected by the metallic oxides; nor have experiments been tried with any definite result as to the employment of tungstic acid, molybdic acid, titanic acid, chromic acid, and chromic oxide, &c.

Genuine rubies and sapphires, crystals of alumina with all the characteristics—chemical and optical—of the natural stones have now been obtained artificially, though of small size.*

Coloured Glass and Glass Staining.—Coloured glass may be considered in two classes —that coloured as a whole, and that only partially coloured. The latter is prepared with such metallic oxides as will impart to the glass very intense colour; for instance, cuprous oxide, cobalt, gold, and manganese oxides. This kind of glass is termed superfine, and is prepared in the following manner:—Two melting vessels are placed in the oven; one contains a lead glass, the other the coloured glass. We will take as an example glass coloured red with cuprous oxide, which if further oxidised imparts a green colour to the glass. The glass blower dips his pipe first into the red glass; and collects a sufficient quantity to blow; then he dips this into the white glass, and proceeds to form a cylinder or roll, as in the making of table glass. Superfine glass is known as "outside" and "double," or "double layer." In the first case the workman takes a lump of white glass upon his pipe and covers it with the coloured glass; or, in the second case, he takes up only a small quantity of white glass, then sufficient of the coloured glass, and again more white glass. Red glass may be obtained with either Cassius's purple, cuprous oxide, or iron oxide as the colouring ingredient. Cassius's purple is used chiefly for ruby-red glass. It was long thought that ruby-coloured glass could not be obtained with any other preparation than Cassius's purple, but twenty-five years ago Fuss showed that gold chloride was effectual. If glass containing salts of gold or cuprous oxide is cooled suddenly, the colour disappears; then if again gently warmed, not quite to softness, the colour suddenly reappears in full splendour. This phenomenon occurs equally in atmospheres of oxygen, hydrogen, and carbonic acid. In the preparation of cuprous oxide glass, lead glass is taken as a basis, to which 3 per cent. of the cuprous oxide is added. The

* In the artificial sapphire the blue colour has been obtained, in the absence of cobalt, by a compound of chromium not yet examined.

drawback to the employment of the protoxide is the readiness with which it becomes oxide, thus imparting a green colour to the glass. To prevent this change, iron filings, rust, or tartar is added, or the glass is stirred with green wood. Copper glass, as has just been said, is colourless on cooling, regaining its colour during the process of annealing. Iron oxide, known commercially as blood-stone, ochre, or red chalk, is also used to impart a red colour. Yellow and topaz-yellow are obtained by means of potassium antimoniate or glass of antimony, silver chloride, borate, and sulphide. Uranium oxide imparts a green-yellow. Blue is obtained from cobalt oxide, more seldom by means of copper oxide. Green results from the addition of chrome-oxide, copper oxide, and ferrous oxide. Violet is obtained from manganese oxide (braunite) and saltpetre; black, from a mixture of ferrous oxide, copper oxide, braunite, and cobalt oxide. A beautiful black results from iridium sesqui-oxide.

For the production of *Satin Glass*, vessels blown of coloured glass are further blown within a metal mould so as to display in a kind of relief depressed stripes, rows of small depressions. Then comes a layer of colourless crystal glass above the coloured glass. It attaches itself to the smooth, level parts, but it does not penetrate into the depressions, which remain filled with air. When the vessel is completed, fitted with handles, feet, &c., and has been cooled down, the outer surface receives a matt polish which gives it a satin-like appearance. The favourite colours for this style are reseda green, heliotrope violet, garnet red, and jonquil yellow.

Painting on Glass.—The delineation of figures and scriptural events in coloured glass dates from a very remote period. At first the work was merely mosaic, pieces of coloured glass being inserted in leaden framework. Glass painting was known in Germany in the Middle Ages, and soon extended throughout Europe. In the thirteenth century, when Gothic architecture became prevalent, glass painting also became more general, as until then the heavy, round-arched windows were too small to admit of ornament. But it was not until the fifteenth century that the heavy outlined figures were discarded for the more mingled colours of heraldic device, as seen in the churches of Sebaldus and Lorenz, of Nuremburg, in the productions of the celebrated Hirschvogel family. This style lasted till the sixteenth century, when the glassmaker tried the effect of pigments upon glass. Since that time the art has gradually developed, the improvement at first being most manifest in France and the Netherlands.

The nature of glass painting or staining is in principle the following:—When coloured glass, rendered easily fusible by the metallic oxide it contains, is finely pulverised, and laid upon a plain glass surface and heated, it forms a skin, or "flash," as it is termed, this skin or layer of glass being said to be "flashed on." It is evident that very brilliant effects may thus be obtained. The near surface of the glass receives the strong shades and colours, the other or distant surface the lighter tints. White was not employed in the older glass paintings, but is now used in the flesh-tints, pure white effects, &c. Tin oxide and potassium antimoniate yield a good white. For yellow, Naples-yellow, or antimony-yellow, or a mixture of the iron, tin, and antimony oxides, or of antimonic acid and iron oxide, of silver and antimony sulphides, or silver chloride is used; for red, iron oxide, purple of Cassius, and a mixture of gold oxide, tin oxide, and silver chloride; for the brown, manganese oxide, yellow ochre, umber, and iron chromate; for black, iridium, platinum, cobalt, and manganese oxides; for blue, cobalt oxide, or potassium-cobalt nitrate; for green, chromium and copper oxides. Two kinds of colours are distinguished, the hard and the soft. The soft are called varnish colours, are very easily melted, forming a kind of glaze upon the glass. These colours are placed upon the outer surface. The hard or decided tints are semi-opaque, and are placed upon the inner surface of the glass. The binding fluid or vehicle is a mixture of silica, minium, and borax, with which the colour, being pre-

viously ground to a fine powder, is intimately mixed. This mixture is painted on the glass with a pencil, and the glass plate is afterwards fired in a muffle. Volatile oils have recently been employed as vehicles—viz., oil of turpentine, lavender, bergamot, and cloves. The burning-in, or firing, the colours was formerly effected by placing the glass tablet with dried and pulverised lime in an iron pan raised to a red heat. But recently the muffle oven has been employed. The bottom of the muffle is covered to a depth of one inch with dry powdered lime, upon which the plate of glass is laid, and again a layer of lime. The oven is then raised equally to a dark-red heat. After six to seven hours the fire is gradually withdrawn, and the oven allowed to cool. The glass is taken out, cleansed with warm water, and dried.

Enamel, Bone Glass, Alabaster Glass.—By enamel is understood in glass manufacture a coloured or colourless glass mass rendered opaque by the addition of oxide of tin. It was formerly prepared in the following manner :—An alloy of 15 to 18 parts tin and 100 parts lead was oxidised by heat in a stream of air, the oxide pulverised and washed. The mixture of the oxides was then fritted with the glass. An enamel-like appearance is imparted to glass by arsenious acid, silver chloride, calcium phosphate, cryolite, fluor-spar, sodium aluminate, and precipitated barium sulphate. Bone glass, so called, is a milk-white, semi-opaque glass, containing calcium phosphate in the shape of white bone-ash, sombrerite, or phosphorite. It is employed for lamp globes and shades, thermometer scales, &c. It is made by adding to white glass about 10 to 20 per cent. of white bone-ash, or a corresponding quantity of mineral phosphate. After melting, the glass is generally clear and transparent, becoming milk-white and opaque during the process of blowing. The colour is finally developed during annealing.

A glass resembling bone glass, but opaque and of as uperior lustre, is the alabaster or opal glass, sometimes known as rice glass. It is merely a preliminary stage in the formation of glass, very rich in silica and imperfectly fused. Its opacity is derived from undissolved particles. The same mixture is used for alabaster glass as for crystal glass; as soon as it is melted it is baled out and chilled. When the next lot is melted the chilled mass is put upon it and worked up together at the lowest possible temperature. The undissolved particles of the melt which cause the turbidity should be only microscopic, and be neither distinctly perceptible grains nor bubbles. This is the great difficulty in the manufacture of alabaster glass, since the impurities as a rule do not disappear until the mass has been thoroughly melted and clarified. Alabaster glass is identical with Réaumur's procelain.

Cryolite Glass (*hot cast porcelain*) is obtained, according to Williams, by melting a mixture of—

Silica	67·19
Cryolite	23·84
Zinc oxide	8·97

An Austrian cryolite glass, according to Weinreb, contained—

Silica	78·00
Alumina	3·12
Ferric oxide	trace
Manganous oxide	trace
Lime	3·87
Soda	9·46
Potassa	4·35
Fluorine	3·77

Ice Glass.—Ice glass is made by plunging the mass of glass attached to the end of the blower's pipe, still at a glowing red heat, into hot water, in which the glass is opened and blown out. It then resembles a mass of thawed ice, with a beautifully pellucid appearance. It is also known as crackle glass; in France, as

verre craquele. Agate glass is obtained by melting together the waste pieces of coloured glass.

Hematinone and Aventurine have already been described.

Muslin Glass is plate glass ornamented with designs in dead white. One method of producing this effect consists in flashing over the surface a thin layer of plumbiferous crystal glass. The other method depends on coating the glass with a coating of enamel. The mixture of the Belgian enamel is 100 parts sand, 110 red lead, 110 parts of cullet (from crystal glass), 35 borax (anhydrous), and 25 parts tin oxide.

Glass relief.—Glass relief is obtained by enclosing a body of well-burnt unglazed white clay, moulded to the required form between layers of lead-glass, the result being similar in appearance to an article in matted silver. Gold matte is imitated by employing a yellow glass. This branch of their art has been known to the Bohemian glass manufacturers for upwards of eighty years.

Iridescent Glass.—Since 1872 articles of glass have been made with rainbow coloured iridescence. Such glass was first obtained by Brianchon by coating the objects (*i.e.*, paper-weights, &c.,) with a flux of auriferous bismuth oxide, so thin that it is almost imperceptible by transmitted light, but in reflected light shows the colours of the spectrum. Whether the observation of Fremy and Clémandot that glass can be made iridescent by treatment with hydrochloric acid under pressure can be applied in practice is still undecided.

Filligree or Reticulated Glass.—By fibre or filligree glass is understood that kind of glass work formed of variously coloured or white opaque glass threads, these threads being sometimes as fine as a single hair. They are generally drawn from tubes or sticks of glass of various colours, heated to redness, and formed into sticks, tubes, or spirals. Two of these tubes are taken, placed together, and blown out into a vessel of the required form,which is characterised by the conformation of the glass threads in the stick. From the spiral network thus formed this kind of glass is sometimes termed reticulated.

Millifiore Work.—Millifiore work is a peculiar form of mosaic glass work, in preparation similar to that of Petinet glass. Small filligree canes of different coloured glass are placed side by side to form a thick cord or column, the cross section of which appears of a particoloured grain. These cords or columns can be twisted to almost any required form, or when heated and drawn out the glass threads of various colours of which it is composed form a single thread of very varied hue and great beauty. These threads again can be worked into ornaments, or formed into lumps or balls. The best kind of millifiore work are the paper-weights, often sold at fancy bazaars as Bohemian glass weights—these are merely lumps or rolls of the many coloured glass thread placed together, heated, and finally coated with a film of clear white glass by being for a few moments held in the white glass melting-pot.

Glass Pearls.—There are two kinds of artificial or glass pearls, namely, solid or massive pearls and blown pearls. The first are known as Venetian pearls, and those made in Venice are preferred, the export from this city in 1868 representing a money value of 7,755,000 francs. The manufacture is chiefly carried on in the Island of Murano. The pearls are made from small glass tubes, either white or coloured. Oxide of tin is employed in the preparation as well as the various metallic oxides for imparting the desired colours.

Solid Pearls.—The glass tubes are cut into small pieces or cylinders. The sharp edges of these cylinders are removed by placing them in an iron vessel brought to a red heat, the beads being constantly stirred with an iron spoon. Previous to this operation the interior or hollows of the beads are filled with powdered charcoal. They are then well washed, dried, and packed. By another mode of preparation. the pieces of glass tubing are placed in a revolving vessel similar to a coffee roaster.

The finished pearls are generally strung, the charcoal being placed in the interior or tube to prevent its closing.

Blown Pearls.—The preparation of blown pearls is quite a distinct manufacture. They resemble the real pearl in form, colour, and surface. Jaquin, a French paternoster or rosary maker, in the year 1656, remarked that when whitings (*Cyprinus alburnus, ablettes*) were washed with water, a residue remained consisting of a beautiful pearly substance. This was the foundation of the manufacture of the artificial pearl. Jaquin scaled the fish, mixed the scales with water, and obtained the celebrated "*Oriental pearl-essence*," or "*Essence d'Orient*," a substance identical with *Guanin*. A small bead of gypsum or other hardening paste is coated with this mixture, dried, and dipped into molten glass, a thin film of which adheres.

The pearl is sometimes round, sometimes pear-shaped, or flat. Another method of preparing the pearls is by means of beads blown from glass tubes of various thicknesses. These beads or small bulbs are then filled with pearl essence. To prepare this essence, say a quantity of 120 grammes, 4000 fish are necessary; thus a pound of pearl essence requires from 18,000 to 20,000 fish for its preparation. The scales are allowed to stand about an hour in water to permit the slimy matter adhering to them to settle; they are rubbed down in a mortar with fresh water, and strained through a linen cloth. Thus prepared the paste is ready for insertion in the glass beads, a little ammonia being added to prevent decay.

Into the red pearls, which are to imitate coral, and into the yellow ones there are blown suitable colours ground up with gum arabic, and into the *marcasite* or mirror pearls there is introduced an easily fusible metallic alloy.

According to Heckert (Petersdorf) a *pearl mosaic* with perforated pearls is made by executing the pearl mosaic in the first place as a kind of embroidery; the front of the pearls is then attached by means of cement or enamel to the objects to be decorated. If a cement is used the tissue and the threads of the embroidery are burnt away after it has hardened. If enamel is used it is melted together with the pearls. The effect is very fine.

Glass Etching.—Etching in glass was discovered in 1670 by Schwankhardt. If powdered fluor-spar is covered with strong sulphuric acid, hydrofluoric acid is given off on the application of heat, which acts upon the silica of the glass so as to form silicon fluoride, which escapes, and water. At the parts acted upon the other constituents of the glass remain as a loose powder, which can easily be removed. The idea of etching upon glass plate designs suitable for printing came from Hann, of Warsaw (1829). More recently, Böttger and Brömeis, with Auer, of Vienna, have improved the processes. The etching-ground used for engraving on metallic surfaces would not in this case give favourable results. Pül recommends a molten mixture of 1 part asphalt and 1 part colophonium, with as much oil of turpentine as will bring the mass to the consistency of a syrup. Etched glass plates have been used by Böttger and Brömeis to print from instead of steel and copper. In the press the glass plate is backed by a cast-iron plate. The process, however, has not been practically successful; it is better suited to the production of bank-notes, &c., than engravings, the resulting etchings being hard in tone. But for purposes of decoration, etched glass is largely used. By the method of Tessié du Motay and Maréchal of Metz, a bath is made of 250 grammes of hydrofluoride or fluoride of potassium, 1 litre of water, and 250 grammes of ordinary hydrochloric acid. Kessler employs a solution of fluoride of ammonium.

Etching for decorative purposes is likewise effected with hydrofluoric acid. According to Tessié du Motay, the acid is best produced in a bath of 250 grammes double hydrogen potassium fluoride, 1 litre water, and 250 grammes ordinary hydrochloric acid. For matte etching and writing on glass, Kessler recommends a solution of ammonium fluoride, which is found serviceable for marking bottles, cylinders, tubes, &c.

For matte etching on glass Reinitzer uses solutions of acid alkaline fluorides. In order that the matte may come up in different tones, where it is desired to obtain the darkest possible tone by reflected light, the practice in the National Glass Painting and Etching Establishment at Budapest is to etch the same spot twice in succession. A single etching gives a lighter tone, and for still lighter tones the surface which has been etched is cleared, once to nine times, with dilute liquid hydrofluoric acid. In this manner they obtain at Budapest eleven gradations. If such an etched plate is examined under a moderate microscopic power, we see a very uniform arrangement of depressions and elevations of a crystalline form. At the margin of the matte surface these crystals are more thinly scattered and better developed, so that their form can be distinctly recognised. Fig. 432 shows the margin of such an etching from the Budapest establishment magnified 450 diameters. The predominant crystals are hexagonal, and quite agree with those of sodium silicofluoride. Besides there are long crystals, very similar to those of calcium silicofluoride. That the crystalline figures are elevated we may readily learn by the phenomena apparent on raising or lowering the tube of the microscope. It may be seen still more plainly if we rub the matte plate over with indian ink and then wipe it superficially with elder pith. All the parts between the crystals will then appear dark under the microscope, while the crystals themselves are colourless. If a plate of potash glass is etched matte there will appear the tesseral crystals of potassium silicofluoride, and in this manner potash and soda glasses might be respectively distinguished.

Fig. 432.



The etchings are the most delicate in presence of potassium salts. If ammonium salts are used the solution should be saturated; less concentrated for sodium salts and more dilute for potassium salts. In all processes for rapid etching ammonium fluoride is in use, and we may easily see that a concentrated solution of ammonium fluoride, acidified with hydrofluoric acid, produces a fine matte in a few seconds.

As regards the proportions of the ingredients in the mixing baths, we can lay down definite formulæ only if the glass is identical in composition. In practice it is sufficient to set out with an approximate formula for glass—*e.g.*, $R_2Si_3O_7$, when R is a monovalent metal. The reaction then ensues according to the equation:

$$R_2Si_3O_7 + 4F_2HNa + 10FH = SiF_6R_2 + 2SiF_6Na_2 + 6H_2O.$$

Hence it appears that for the complete utilisation of the sodium fluoride there must be present a considerable quantity of free hydrofluoric acid. But as this hydrofluoric acid may easily prove injurious, it is better to use some other acid to saturate the bases.

Acetic acid is the most suitable, as it does not decompose the acid fluorides and liberate hydrofluoric acid. The process then takes place according to the equation:

$$R_2Si_3O_7 + 9F_2HNa + 5C_2H_4O_2 = SiF_6R_2 + 2SiF_6Na_2 + 5C_2H_3O_2Na + 7H_2O.$$

We see that free hydrofluoric can never occur in this process, and further, that the solubility of the silico fluoride is diminished by the sodium acetate which is formed. From the last equation we see that the proportion of sodium fluoride to acetic acid is 93 : 50, or approximately 9 : 5. On the basis of the second reaction we should have

the following composition: 30 parts hydrofluoric acid (50 per cent.), 17 sodium acetate and soda-ash, 9 or 23·4 soda crystals.

Matte etching with gaseous hydrofluoric acid yields very unequal results. It is unfit for surfaces, and can serve only for line-drawings.

Sand-Blast Machine.—C. Tilghman, in working glass, uses a current of sand projected forcibly against the surface of the object to be etched. The sand derives its velocity from air or steam. Whilst brittle bodies are attacked by the current of sand, elastic bodies are able to resist it, and hence stencil-plates of caoutchouc can be applied to the object. The parts left uncovered are ground by the sand, thus forming a design.

EARTHENWARE OR CERAMIC MANUFACTURE.

Weathering.—In consequence of the reactions between the solid crust of the earth and the atmosphere the masses of rock are gradually destroyed and broken up. The causes of this weathering are partly mechanical, partly chemical. Among the former are changes of temperature, especially frost, the mechanical power of falling water (rain, streams, &c.); the chemical includes the action of atmospheric oxygen, of carbonic acid, and of water.

The water absorbed by rocks becomes, in consequence of the formation of ice during the cold season, a powerful agent for the disaggregation of the superficial strata. Of more importance are the chemical changes in rocks; oxygen converts sulphides into sulphates and ferrous into ferric compounds. Water forms, with numerous substances, hydrates and silicates, with an accompanying increase of volume, and converts anhydrite into gypsum. By the prolonged action of water even the more permanent minerals, such as felspar, are decomposed and their ingredients are rendered soluble. Carbonic acid in watery solution dissolves the carbonates present in rocks (iron-spar, limestone, dolomite, &c.) and phosphates (apatite, phosphorite).*

The final result of weathering is always mechanical comminution and chemical decomposition in such a manner that a portion of the constituents is dissolved in water. The residue either remains in heaps at the place where it was formed, or it is conveyed away and subjected to a process of elutriation by the action of water, the coarser and heavier matter being separated from the finer and lighter.

Clays and their Application. Felspar.—To the most important alumina combinations found native belongs felspar. This mineral is one of the chief members of the class containing gneiss, granite, and porphyry. Potash-felspar, $\left.\begin{matrix}3Si\\AlK\end{matrix}\right\}O_8$, with 65·4 parts of silica, 18 alumina, and 16·6 potash, is also known as *orthoclase* or *adularia;* when sodium takes the place of potassium, the felspar *albite* is formed. According to Mitscherlich some felspars contain 0·4 to 2·25 per cent of barium. When felspar is under the influence of water and carbonic acid with changes of temperature, it loses its potassium silicate, which being washed out, the potash is taken up by plants, and will perhaps account for some portion of the potash always present in their ash; some of the silicate is acted upon by carbonic acid, by which the silicic acid is separated and soluble potassium carbonate formed. In following this decomposition to a conclusion, we may surmise that the silicic acid thus set free becomes a constituent of the opal and chalcedony spar. All clays are essentially aluminium silicate; and, in many instances, as in Devonshire and Cornwall, the change from felspar of the fine white granite to clay by disintegration is very perceptible. By washing this clay to free it from quartz and mica a fine white clay is obtained, known as kaolin or porcelain clay. Again, by

* Biological agents take a part in the work which is not yet fully recognised; lichens secrete oxalic acid and corrode the rocks upon which they grow, and microscopic plants exert a more varied and profound influence.

washing with potash lye, whereby the free silica is taken up, there is obtained, in most cases, a fine plastic mass, consisting of 1 mol. of alumina, 1 mol. of silica, and 2 mols. of water. The quantity of free silicic acid varies between 1 and 14 per cent.

The weathering of the felspar may be formulated thus—

$$1 \text{ mol. felspar, } Si_3O_8KAl, \text{ or } \left.\begin{matrix}3Si\\AlK\end{matrix}\right\}O_8,$$

gives, under the influence of water,

1 mol. porcelain clay, $2SiO_4HAl$, and

1 „ acid potassium silicate,

the latter forming a soluble combination similar to water-glass. Porcelain clay occurs in the following localities:—1. Bavaria: Aschaffenburg, Stollberg, Diendorf, Oberedsdorf. 2. Prussia: Morl and Trotha, near Halle (material for Berlin porcelain manufacture—decomposed or disintegrated porphyry). 3. Saxony: near Schneeberg and Misnia. The first is a weathered granite; the latter, porphyry. 4. Eastern Hungary; Brenditz in Moravia; near Carlsbad, Bohemia; Prinzdorf in Hungary. 5. France; St. Yrieux, near Limoges. 6. England: St. Austell, in Cornwall. Weathered granite: a mixture of orthoclase and quartz. It is found chiefly on Tregoning Hill, near Helston. 7. China. It naturally follows that the clay should contain foreign substances; and it is from the quality and quantity of these substances that the several varieties of clay are obtained, of course with due reference to the chief constituents—silicic acid and alumina. The purer clays contain generally the following foreign substances:—Sand, partly as quartz sand, as potassium silicate, and partly as particles or fragments of undecomposed minerals; baryta combinations; magnesium carbonate; calcium carbonate; ferric oxide; sulphur pyrites; and organic matter.

In the examination of clays, Seger treats the sample with concentrated sulphuric acid. The clayey matter is decomposed, while quartz and felspar remain untouched. The kaolins named below have the following composition:—

Components.	Kaolin from Ledetz.	Kaolin from Kottiken.	Kaolin from Tremosna.	Kaolin from Zettlitz.	Kaolin from Lettin.	Kaolin from Kaschkau.	Kaolin from Sennewitz.	From Royal Porcelain Works.
Clayey matter	88·26	87·41	90·29	96·55	74·09	78·51	63·77	54·92
Quartz	3·08	6·40	4·08	2·30	17·21	20·90	35·50	23·52
Felspar	8·66	6·19	5·63	1·15	8·70	0·59	0·73	21·56
Composition of the Clay—								
Silica	45·36	44·76	45·98	45·36	45·63	45·00	45·30	45·46
Alumina	39·58	39·65	39·36	39·71	38·08	39·32	37·15	37·35
Ferric oxide	0·92	0·72	0·73	1·13	0·88	0·75	1·29	1·07
Magnesia	0·20	0·34	0·45	—	0·66	0·28	0·78	0·73
Potassa	0·21	0·02	0·99	1·24	1·84	0·53	2·02	2·57
Water	14·02	14·07	13·28	13·32	13·32	14·20	13·11	12·74

Technical Qualities of Clays.—For the technical application of the clays the important qualities are colour, plasticity, and hardening well under heat.

Colour.—Naturally clays are white, yellow, blue, or green. Pure clay is white; coloured clays are the result of several admixtures. White clay contains but a small quantity of ferrous oxide, and becomes after burning yellow or red; these colours originating from the organic substances disappear on their being volatilised after many firings. The coloured clays change their colour during firing, becoming red or red-yellow. Fine clays are prepared only from those becoming white by continued burning.

Plasticity.—The clay should absorb water readily, forming a tenacious mass, capable of taking sharp and clear impressions. It is evident that the plasticity of the clays

depends in a great measure on their composition. Sand is the constituent most prejudicial to plasticity, lime less so, and oxide of iron least of all. Clay possessing a high degree of plasticity is said to be *fat* or *long*, and when in the opposite condition *lean*, *thin*, or *short*. All *shrunk* clays, that is, all clays decreased in volume by burning, are said to be either *drawn* or *burst*. The amount of shrinkage depends of course upon the quantity of water the clay contains; the same kind of clay does not always exhibit the same shrinkage. Fat clays shrink more than short clays. The diminution in surface by shrinkage varies between 14 and 31 per cent. the capacity or solid contents between 20 and 43 per cent. Clay may be burnt so hard as to give sparks when struck with steel; but its property to form a plastic mass with water is then wholly lost. Pure clay (aluminium silicate) is by itself infusible, but by mixture with lime, ferric oxide, and other bases, it becomes more or less easily fusible. According to the experiments of E. Richters (1868) the refractory qualities of clay are least influenced by magnesia, more so by lime, still more by oxide of iron, and most by potash. Fusible clay obviously is not adapted to the manufacture of porcelain or such ware as is likely to be exposed to a high temperature. A fusible and a refractory clay, when heated together, combine into a mass that does not cleave to the tongue. By the manufacture of clay ware, then, is understood the binding of certain clays together by means of a suitable flux.

Kinds of Clay.—The clays employed in ceramic manufacture are—

1. Refractory clays; as porcelain and plastic clays.
2. Fusible clays; as potter's clay.
3. Limey clays; as marl, loam.
4. Ochre clays; as ruddle, ochre.

Of these porcelain clay is the most important; it is of various colours, very tenacious, plastic to a high degree, burns white, and is not fusible in a porcelain-oven fire. It is ordinarily found in the tertiary formation, almost always accompanied by other kinds of clay, by quartz-sand, and by brown coal. For practical purposes it is important to know that clays of the same strata and of the same pit often differ largely in their refractory property. This knowledge is not only the result of experience, but of a lengthy series of experiments made by C. Bischof, Otto, and Th. Richters. The strata near Klingenberg-on-the-Maine, at Coblenz, Cologne, Lautersheim, and Vallendar-on-the-Rhine, Weisbach in Baden, Bunzlau in Silesia, Schwarzenfeld near Schwandorf, and Kemnath in Bavaria, in the province of Hessen, in Saxony, in Belgium, near Dreux in France, and Devonshire and Stourbridge in this country, are all celebrated for this clay.

As plastic clays may be mentioned the white clays of Ebernhahn (1), Baumbach (2), Bendorf (3), Lämmersbach (4), and Höhr (5), all from the so-called Kannenbäckerland, Germany; as well as a lean (6) and a fat (7) white clay of French origin.

Constituents.	1.	2.	3.	4.	5.	6.	7.
Clay substance	71·22	76·30	39·71	66·23	54·73	44·63	71·54
Quartz	24·03	22·40	57·15	31·42	41·77	52·77	25·97
Feldspar residues	4·75	1·30	3·14	2·35	3·50	2·60	2·49
Components of Clay substance—							
Silica	46·62	47·44	47·44	47·39	47·45	45·99	45·75
Alumina	36·01	37·21	35·74	36·40	37·88	38·08	35·77
Ferric oxide	1·39	1·68	1·94	1·52	1·41	2·44	2·94
Lime	—	trace	trace	—	—	trace	—
Magnesia	0·73	0·79	0·88	0·51	0·71	1·19	0·78
Potassa	3·47	4·22	3·85	3·96	4·08	2·36	1·24
Loss on ignition	10·19	9·69	9·52	9·92	9·00	10·76	13·70

The chemical composition does not enable us to judge of the sharply-marked differences in the degree of plasticity, which is very low in kaolins even when the proportion of pure, hydrated aluminium silicate is high. Hence the property of plasticity does not belong to any peculiar chemical compound, but seems to fluctuate in clays of similar chemical composition, according to degree of mechanical subdivision and to the molecular arrangement. Possibly the degree of plasticity may be determined by the structure of the rocks from which the clay has originated.

The following analyses show the composition of certain fire-clays (refractory clays):—

	1.	2.	3.	4.	5.
Silica	47·50	45·79	53·00	63·30	55·50
Alumina	34·37	28·10	27·00	23·30	27·75
Lime	0·50	2·00	1·25	0·73	0·67
Magnesia	1·00	—	—	—	0·75
Ferric oxide	1·24	6·55	1·75	1·80	2·01
Water	1·00	16·50	—	10·30	10·53

1. Almerode in Kurhessen (crucible). 2. Schildorf near Passau (graphite crucible). 3. Einberg near Coburg (porcelain capsule). 4. Stourbridge. 5. Newcastle (fire-brick).

The composition of the Stourbridge fire-clay will be seen from the following analyses by Sir F. A. Abel, F.R.S., Chemist to the War Department:—

Sample.	Silica.	Alumina.	Ferric oxide.	Alkalies, Waste, &c.
1	66·47	26·26	6·63	0·64
2	65·65	26·59	5·71	2·05
3	65·50	27·35	5·40	1·75
4	67.00	25·80	4·90	2·30
5	63·42	31·20	4·70	0·68
6	65·08	27·39	3·98	3·55
7	65·21	27·82	3·41	3·56
8	58·48	35·78	3·02	2·72
9	63·40	31·70	3·00	1·90

The sample No. 9 containing only such a small quantity of iron, is much superior to No. 1, whose refractory properties may be doubted. The clay is dug from pits varying from 120 to 570 feet in depth. It is generally found below three workable coal measures, between marl or rock and an inferior clay. The seam averages 3 feet in thickness, and never exceeds 5 feet, while the middle of the seam contains the clay selected for crucibles, &c. Pot-clay or crucible-clay only occurs in small quantities, and costs at the pit-mouth 55*s.* a ton, ordinary fire-clay only realising 10*s.* a ton.

Potter's Clay.—Ordinary potter's clay also possesses most of the properties of plastic clay; many varieties form with water a similarly tenacious mass. But potter's clay is highly coloured, retaining the colour after burning. It effervesces on the application of hydrochloric acid and forms the transition to marl. It follows from its containing large proportions of lime and oxide of iron that it is fusible, and melts according to the quantity of these constituents at a higher or lower temperature into a dark coloured, slag-like mass. It is found in the last formation, or entirely on the surface of the earth, and sometimes in the tertiary formation. It contains among other foreign substances organic matter, iron and other pyrites, gypsum, &c.

Fuller's Earth is a soft, friable mass, formed by the weathering of diorite. In water it falls to a powder, not forming a plastic pulp. It is used for removing grease-spots from paper, &c., and was formerly employed in fulling cloth, whence its name. It is also used in paper-making, and as an addition to ultramarine. It contains

a small proportion of alkali, but its detergent action depends on its mechanical texture.*

Marl.—Marl is a mechanical mixture of clay and calcium carbonate, containing sand (sand-marl) and other constituents; that containing lime is called lime-marl; that clay, clay-marl. In water it falls to powder, and forms a non-adhesive, pasty mass. With acids it effervesces, whereby more than half the weight is lost. It melts easily. It is found in the lias and chalk formation. Its chief application is to the improvement of land.

Loam.—Loam may be considered as the result of the mixture of clay with sand. It is a clay more or less mixed with quartz-sand and iron-ochre, also with lime, when it assumes a yellow or brown colour, changing on burning to a red. It forms with water a slightly plastic mass, and is not very refractory. It is found always on the surface of the earth, and known as common clay, employed in the manufacture of bricks, coarse pottery, &c.†

Two brick-clays, belonging to the cretaceous formation, near Hanover, had the following composition when dried at 120°—

	Stöcken.		Lindener Hill.	
	Total.	Insoluble in H_2SO_4.	Total.	Insoluble in H_2SO_4.
SiO_2	54·01	18·81	59·91	37·17
Al_2O_3	27·98	0·68	17·96	1·79
Fe_2O_3	2·10	trace	1·09	trace
CaO	2·85	—	8·21	trace
MgO	0·65	—	0·41	—
Alkalies	0·68	—	0·41	—
CO_2	1·94	—	6·02	—
SO_3	0·56	—	0·46	—
H_2O	9·03	—	5·64	—
	99·80	19·69	100·11	39·30

If, according to Seger's proposal, we consider the part soluble in sulphuric acid as the true clay substance, and consider that for each 1 part alumina 3·51 silica belong to the felspar, we have the composition—

Components.	Stöcken.	Lindener Hill.
Quartz	16·42	30·90
Felspar remnants	3·27	8·40
Actual clay	80·31	60·70
Components of Actual Clay—		
SiO_2	43·83	37·21
Al_2O_3	33·99	26·46
Fe_2O_3	2·61	1·77
CaO	3·55	13·43
MgO	0·80	0·67
Alkalies	0·84	0·67
CO_2	2·42	9·83
SO_3	0·70	0·73
H_2O	11·26	9·23

As further calcium carbonate and sulphate do not belong to the true clay, and as the former has an influence on the burning, they are to be mentioned separately:—

* It is found near Reigate (Cormonger's Farm), in Surrey; near Maidstone, in Kent; Woburn, in Bedfordshire; Old Town, near Bath; and in the north-east of Ireland.

† In horticultural works the word loam is used in a totally different sense to signify the mass resulting from the decomposition of grass sods, pared off from the ground and laid up in heaps.

Components.	Stöcken.	Lindener Hill.
Quartz	16·42	30·90
Felspar remains	3·27	8·40
Calcium carbonate	4·45	14·10
„ sulphate	0·95	0·82
Actual clay	74·91	46·78
Components of Actual Clay—		
SiO_2	46·96	48·83
Al_2O_3	36·42	34·81
Fe_2O_3	2·80	2·37
MgO	0·87	0·89
Alkalies	0·91	0·89
H_2O	12·04	12·21

Certain clays contain also manganese, cobalt, barium, titanium, vanadium, molybdenum, gold, and cerium.

Behaviour of Clays in Working.—Clays lose their water partly on drying, when they undergo a linear shrinkage of 11·5 per cent., and partly at a higher temperature. On losing this water of hydration at a red heat clay loses permanently its plasticity and forms a stony, very porous, and friable mass. At higher temperatures it becomes denser, harder, sonorous, but still has an earthy fracture. The silica expels the carbonic acid, chlorine, and sulphuric acid, forming silicates with the alkalies, lime, magnesia, and ferric oxide. These silicates form with the aluminium silicate double silicates, which are easily fusible. The clay sinters more and more, and finally melts. Though the specific gravity of the clayey substance rises at a dull red heat from 2·47 to 2·70, and then falls at a white heat to 2·48, the density of the entire bricks increases with the rise of temperature by the loss of the pores. According to Karmarsch, newly moulded bricks of 262 millimetres long, 130 broad, and 51 millimetres thick, shrink per cent.:—

———	Length.	Breadth.	Thickness.
On drying	7·25	10·75	9·75
„ drying and slight burning	8·50	13·00	14·75
„ burning to clinkers	11·75	23·00	19·75

Aron observed a linear shrinkage of from 0·3 to 4·1 per cent. at redness, and of 12 to 8 per cent. at whiteness. The less the bricks shrink the coarser the grains of sand which they contain.

Experiments by Daube show how much the porosity and the resistance of bricks moulded from the same clay depend on the temperature. The results are given in the following table:—

———	Slightly burnt.	Medium burnt.	Hard burnt.	Clinkers.
Moisture taken up on dipping in water, per cent.	16·2	16·5	16·4	1·6
Do. in boiling water	18·0	19·3	19·0	2·6
$CaSO_4$ dissolved in water	0·7	0·2	0·15	0·09
Loss of weight in 10 per cent. HCl	8·5	8·0	7·4	2·5
Do. in nitric acid	5·0	4·9	4·0	0·6
Increase of weight in sulphuric acid by formation of $CaSO_4$	1·2	1·2	0·9	0·8

After treatment with HCl the light- and medium-burnt bricks had strong fissures; those hard burnt only fine fissures, and the clinkers none at all.

The presence of calcium carbonate in fragments or coarse grains is very injurious in fire-clays. According to Seger clays are, indeed, used containing as much as

30 per cent. of calcium carbonate, but such clays, especially if lightly burnt, have a great tendency to weather. This explains why the clays which burn red and which contain little or no calcium carbonate are preferred for roofing tiles, whilst the calcareous clays which burn yellow have been found quite useless. Calcareous clays are, indeed, easier to work, but as they lose in burning not merely water but carbon dioxide, they yield porous bricks. The temperature at which the pores are closed and a dense, porcelain-like mass is produced, lies very near to that at which the mass melts to a slag, and great experience is necessary to prevent the bricks from slagging. Hence, in burning such clays it is necessary to avoid a strong heat. The bricks in consequence retain their porosity and absorb water eagerly. A really weather-proof brick cannot be obtained from clays which contain upwards of 10 to 15 per cent. calcium carbonate.

Changes of Colour in Burning.—Considerable importance often attaches to the property of calcium carbonate to give a yellow or yellowish-green colour on burning to the common ferruginous clays. Whilst pure clay burns white it is turned a red by ferric oxide, the darker as the heat applied is stronger. If the heat is still raised the colour becomes greenish, and finally black, according to Remole, by the partial formation of ferrous oxide. If the ferruginous clay contains at the same time calcium carbonate it will be red, if slightly burnt, flesh-coloured, whitish to dark yellow at incipient sintering, owing to the formation of a yellowish basic silicate of lime and ferric oxide, and green to black on full nitrification. According to Seger this yellow colour appears distinctly if to every per cent. of ferric oxide the clay contains at least 3 to $3\frac{1}{2}$ per cent. calcium carbonate. The yellow colour appears at a lower temperature and is lighter the more the proportion of calcium carbonate exceeds this minimum, appearing at a higher temperature and verging more upon a yellowish-red or yellowish-brown on approaching the proportion above given. If the amount of lime is still lower it merely reduces the red without producing a yellow.

Efflorescences.—After a time bricks, especially if lightly burnt, often show whitish, yellow, green, and even black eruptions. White eruptions generally consist of magnesium, calcium, and sodium sulphates, sodium chloride or bicarbonate, which are either present in the clay or have been introduced by the water, the mortar, or the cement.

Green eruptions upon light-coloured bricks in moist places consist chiefly of algæ, or they may be due to the presence of chrome. Facing-bricks made of the lignitic clays near Wittenberg, displayed, sometimes on their entire surfaces, sometimes only in spots, especially at the corners, a very intense golden-yellow colour, which if examined with a lens was found to consist of mammillary protuberances, in part of a bright grass-green or yellowish-green. Some such bricks contained 0·16 per cent. of soluble salts, consisting of :

Potassa	19·82	Molybdic acid	1·12
Soda	3·17	Sulphuric acid	15·70
Lime	3·24	Silica	2·07
Magnesia	3·34	Chlorine	2·63
Alumina and ferric oxide	0·77	Water	18·25
Vanadic acid	29·43	Insoluble matter	0·46

These coloured eruptions consisted, therefore, chiefly of potassium vanadate, the yellow colour of which is partially modified to green and blue by molybdic acid. Reducing combustion gases and high temperatures make the vanadium compounds insoluble.

Black spots are due chiefly to fungi, which attach themselves where calcium carbonate and sulphate effloresce out of the brickwork.

In addition to the composition of the clay and the temperature of the kilns, the nature of the combustion gases has an influence upon the colour of the bricks.

Seger showed that the dark-red colour of the surface of yellow bricks is occasioned by the absorption of sulphuric acid from the sulphur of the fuel. The moisture precipitated from the combustion-gases of the Berlin Porcelain Works contained per litre:

	Wood furnace.		Gas furnace.
Hydrochloric acid	39	...	114
Sulphuric acid	153	...	384
Phosphoric acid	73	...	—
Ferric oxide and alumina	8	...	17
Lime	11	...	39
Magnesia	8	...	18
Potassa }	38	...	37
Soda }		...	106
Ammonium chloride	—	...	47

At higher temperatures, and on exposure to the action of reducing gases, the sulphuric acid is expelled and the normal colour restored. A yellow brick which had been ignited to redness was uniformly yellow within, but was dark-red on those parts of the surface which had been most exposed to the combustion-gases. The red colour had only penetrated into the brick to the depth of 2 to 3 millimetres. A comparative analysis of the red (I.) and the yellow (II.) parts showed:

	I.		II.
Silica	53·96	...	57·55
Alumina	10·29	...	11·98
Ferric oxide	6·25	...	10·05
Magnesia	1·76	...	1·51
Lime	16·70	...	17·85
Sulphuric acid	11·10	...	0·88

Some red colorations seem to be due to volatile compounds of iron.

The action of the other constituents of the combustion-gases upon the colour of clays has been examined by Seger.

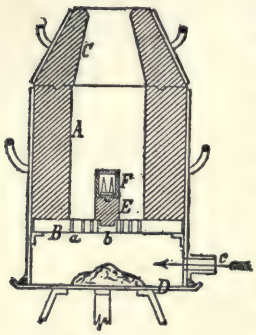
Clays containing iron and lime, and burning yellow if the combustion-gases contain an excess of oxygen, are turned at a red heat a dirty red colour, then flesh colour, and at full redness yellow with a brownish cast. Reducing-gases (hydrogen, hydrocarbons, carbon-monoxides) effect a blackening which, on access of air, gives place to redness. After a preceding reduction, the colours produced by the action of oxygen are lighter, and incline more to a whitish or yellowish-green than if there had been no previous reduction. An occasionally reducing flame in the furnace contributes to develop the light colour of the calcareous clays. Ferruginous clays free from lime turn to a pure red in an excess of oxygen, this the more decidedly the higher the temperature. Reducing-gases change this red colour to a velvet black by the reduction of the ferric oxide to ferrous oxide and metallic iron. If such black bricks are ignited in the air the red colour returns, but not so finely as with an exclusively oxidising flame, so that here to obtain pure colours the action of reducing-gases must be avoided. Clays free from lime and poor in iron, and turning white or yellow, are also blackened by the action of reducing-gases. The clay of Greppin, on exposure to pure hydrogen, after ignition to dull redness, became a light ash grey, and contained 1·69 per cent. ferric oxide and 1·01 per cent. ferrous oxide, after prolonged heating to bright redness it was a dark ash grey, and contained 1·81 per cent. ferric oxide and 0·34 metallic iron. This grey colour very quickly disappears again on the admission of air, but the original colours return, only in a much fainter degree. The flesh colour which characterises the lower temperatures is converted into a whitish yellow, whilst at stronger heats there appears a pure yellow. Clays poor in iron, which burn white in an excess of oxygen, are turned light grey by reducing-gases, and on ignition in the air they become white again.

Infusibility.—C. Bischof and Seger have made comprehensive experiments on the

influence of the composition of a clay upon its behaviour at high temperatures. Bischof holds that the fusion of clays consists in the formation of double silicates and aluminium silicates on the one hand, and a silicate on the other which may have for its base either magnesia, lime or iron, potassa or soda. Pure aluminium silicate is infusible in our ordinary fires, especially if it contains alumina in excess. If one of the above-mentioned bases is present, its fusibility increases with the quantity of the base. If we calculate from the complete analysis of a clay how much alumina comes to one equivalent of fluxing agent, and how much silica comes to one equivalent alumina, the quotient obtained by dividing the latter value by the former will be proportional to the infusibility. On the other hand, Seger maintains that if it were possible to infer the fusibility of a clay from its composition, this could be practicable only if it could be brought into a chemically homogeneous mass.

For the *experimental determination of the behaviour of a clay under heat*, specimens must be ignited. For this purpose Seger recommends the Deville furnace, Fig. 433. In it there is laid a thick wrought-iron plate *B*, beneath the hollow fire-clay cylinder *A*, which is surrounded with a sheet-iron screen. The cylinder, 11 centimetres in width and 20 centimetres in height, is continued by a fire-clay cap *C*, likewise enclosed in iron. The plate *B* is perforated in three concentric rings, with apertures of 5 to 6 millimetres in width, *a*. In the middle is a large hole, *b*, of 30 millimetres in width. The lower part of the sheet-iron screen is closed below with a round iron plate, *D*, which can be luted on air-tight with clay. The air forced in through the pipe, *c*, enters the fire-box through the holes, *a a*, whilst the wider aperture, *b*, serves to receive the support of the crucible, which for this purpose has a plug-like elongation below, fitting into *b*. The same aperture serves to clean out the furnace after use. On the support stands a crucible of 40 millimetres outside diameter and 45 millimetres height, also centred with a small plug at the bottom. This crucible receives the samples of clays to be tested, together with the normal clays, made up in the form of small tetrahedral or prismatic pieces. The crucible, its support, and the cylinder are all made of a mixture of equal parts of Zettlitz kaolin and Neuroda slaty clay. Along with the cones a piece of platinum wire is placed in the crucible. Some burning charcoal is placed in the furnace and retort-graphite from the gasworks, which is preferable to coke on account of its small yield of ashes. Air is forced in at *c* until the melting-point of platinum is reached. The appearances presented by the clays are then examined, and their position with respect to the normal samples is determined.

Fig. 433.



As a scale, Bischof uses a series of neutral clays, the slatey clay of Saarau, the kaolin of Zettlitz, the clays of Stroud-Maiseroul, Mülheim, Grünstadt, Oberkaufungen, and Niederpleis. A further normal point is the fusion of platinum to boiling. The standard clays of the quality used by Bischof cannot be obtained by purchase. The fusion of platinum gives no certain indication, for platinum, like iron, can under certain circumstances absorb carbon from the combustion-gases and thus alter its melting-point. Seger, on the other hand, has prepared tetrahedra of definite composition, which are to be obtained at any time from the Royal Porcelain Works at Charlottenburg.

The Production of Earthenware.—The assertion of the Chinese that they had invented porcelain 3000 years ago is scarcely accurate. It is first mentioned in the ninth century under the name Yao. A century later they learnt the use of a blue colour underneath the glaze. This improvement appeared of such importance that porcelain so adorned was reserved for the exclusive use of the Emperor. No one was allowed to buy such porcelain articles, or even to look at them! In the thirteenth century

porcelain vessels were first decorated with turquoise, yellow, and violet, on coloured grounds, and even with painted designs. Under the Emperor Ching-hoa (1465–1488) a method was discovered of decorating glazed porcelain vessels with coloured designs, often with splendid paintings, in which a green colour predominated. In the fifteenth period, down to 1726, a purple-red pigment was introduced. But towards the end of this period the keramic art of China began to decline. Their material is still, however, excellent in quality, though the Japanese have outstripped them in the decoration of their earthenware. Satsuma, especially, produces splendid vases.

Classification of Earthenware.—Clay ware is generally separated into *dense* and *porous* ware. The dense ware is so strongly heated that half its mass is lost; its fracture is glazed and conchoidal; it is translucent and compact, being impenetrable to water; and it gives a spark when struck with steel. Porous clay ware is, in the mass, not glazed, its fracture open and earthy; and, when not superficially glazed, water freely percolates through it. It also clings to the tongue. The burnt mass, whether dense or porous ware, either remains rough or is glazed.

The following are the essential varieties of clay ware:—

I. *Dense Clay Ware.*—A. Hard porcelain. The mass equal throughout; not indented with a knife; fine-grained, translucent, sonorous, and white. Fracture, fine-grained, and conchoidal. Sp. gr. = 2·07 to 2·49. It may be considered as composed of two substances—namely, a natural clay or true kaolin, infusible, and preserving its whiteness under a strong heat; and a flux consisting of silica and lime, or felspar with or without gypsum, chalk, and quartz. The glazing is essentially due to this flux, and not to lead or tin oxide. It is characteristic of the manufacture of hard porcelain that the burnings are concluded in *one* operation.

B. Soft or tender porcelain. The mass more easily fluid than hard porcelain. Two kinds are known:—

a. French porcelain, a glass-like mass, essentially a potassuim-aluminium silicate, prepared with the addition of clay, therefore erroneously termed a clay ware, and containing lead similarly to crystal glass.

β. English soft porcelain. The mass similar to kaolin, plastic, remaining white when burnt (pipe-clay). It is made with a vitreous grit, consisting of gypsum, Cornish stone (weathered pegmatite), bone-ash (essentially calcium phosphate), in very varied proportions. The glaze is obtained by pulverised Cornish stone, chalk, powdered fire-clay, and borax, mostly with, seldom without, the addition of lead oxide. The glazing is a second process.

C. Statue porcelain, or biscuit ware:—

a. Genuine and unglazed porcelain.

β. Parisian porcelain, or parian. Unglazed statue porcelain is similar to English porcelain.

γ. Carrara, less translucent than parian, and sometimes of a whiter colour.

D. Stone ware. Dense, sonorous, fine-grained, homogeneous, only slightly, if at all, translucent, white or coloured.

a. Glazed porcelain stoneware. Plastic, remaining white after burning, slightly refractory with the addition of kaolin and fire-clay; a felspar as flux; the glaze contains borax and lead oxide.

β. White or coloured unglazed stoneware. Wedgwood ware.

γ. Common stoneware (salt-glazed). No fluxing material is employed, but the firing is increased. Glazed with siliceous soda-alum.

II. *Porous Clay Ware.*—A. Fine Fayence with transparent glaze. The body earthy, clinging to the tongue, non-transparent, sometimes sonorous; the glaze containing lead, borax, felspar, &c.

B. Fayence, with non-transparent glaze. The body of a yellow burnt potter's clay

or clay-marl, with non-transparent white or coloured glaze or enamel, containing tin. To this class belongs majolica, delft ware, &c.

C. Ordinary potter's ware. The body of ordinary potter's clay, or clay-marl, red, coloured, soft, and porous. Mostly glazed with lead, the glaze being always non-transparent. According to the colour of the glaze, the ware is distinguished as white and brown.

D. Plate, terra-cotta, fire-clay ware, tubes, ornaments, vases, &c. The body earthy; mostly more or less unequal; always coloured, porous, easily fluid, and slightly sonorous. Is not usually glazed.

I. Hard Porcelain.—*Grinding and Mixing the Material.*—Hard porcelain is composed of a mixture of colourless porcelain clays with felspar as a flux, which sometimes is composed of quartz, chalk, or gypsum. The porcelain clay, in itself infusible, and becoming in the fire only an earthy, opaque mass, when intimately mixed with the flux material, melts easily at a higher temperature than that of the glass oven. The materials of porcelain manufacture are not found native in such a condition that they may at once be employed; they must be ground to a fine powder, and this washed to separate the foreign substances. Pure kaolin, however, is not utilisable in porcelain manufacture, as it becomes much decreased in volume on the application of heat. It is therefore mixed with fine washed quartz sand, although this addition somewhat impairs the plasticity. This mass on treatment with fire would be porous, and felspar is added to close the pores and to form a binding glass. The proportions in Berlin porcelain, according to G. Kolbe (1863), are 66·6 parts silica, 28·0 parts clay, 0·70 part ferrous oxide, 0·6 part magnesia, and 0·3 part lime.

Proportions of the material as employed at—*α.* Nymphenburg; *β.* Vienna; *γ.* Meissen:—

α.	Kaolin from Passau	65
	Sand therewith	4
	Quartz	21
	Gypsum	5
	Broken biscuit ware	5
b.	Kaolin from Zedlitz	34
	Kaolin from Passau	25
	Kaolin from Unghvar	6
	Quartz	14
	Felspar	6
	Broken ware	3
c.	Kaolin from Aue	18
	Kaolin from Sosa	18
	Kaolin from Seilitz	36
	Felspar	26
	Broken ware	2

The mixture of the materials in the required proportion takes place in large vats, whence the thin pulp is pumped and forced through sieves into another vessel.

Drying the Mass.—After the water is removed from the sediment at the bottom of the vat or tank, the clay appears as a slime, which has to be dried to the required consistency. The drying or evaporation of the water is effected in wide wooden tanks exposed to a strong current of air. This is a very general method of drying the mass, but can only be employed during the summer months on account of the dampness of our climate. It is not, therefore, sufficiently extensive for large manufacturers, and consequently other means of drying are resorted to—usually by means of absorption, the mass being laid on a porous layer of burnt lime, gypsum, &c. Drying by means of gypsum is expensive, as it soon becomes hardened, and has to be removed. The mass can also be dried by means of air pressure, being in this case placed in flat porous boxes,

under which a vacuum chamber is situated. Talbot's apparatus is formed on this principle. In Grouvelle and Honore's system of drying, the water is first partially removed, by means of draining over gypsum, and the mass is then put into firm hempen sacks, which are subjected to pressure in a screw or lever press. Pressed clay has greater plasticity than that dried by artificial heat; but the method is expensive, as the sacks soon require replenishing, being speedily worn out by the constant pressure.

Kneading the Dried Mass.—When the mass is dried by pressure or by absorption, the water in all cases is not equally expelled, and there are also air-bubbles which must be removed. This is done by kneading and treading the mass with the feet and hands, and by this means also the plasticity of the mass is improved. Another method of improving the plasticity is by allowing the moist clay to stand till it becomes putrid. Stagnant water is often employed. Brongniart explained the action of this rotting, as it is termed, to be that gases were formed in the body of the clay, and that by the continuous movement caused in their endeavour to escape, the finest particles of the materials were intimately mixed. Salvétat gives the following hypothesis:—By the rotting there is formed in the mass a large quantity of sulphuretted hydrogen gas. This gas effects the reduction of the alkaline sulphides to calcium sulphides under the influence of the organic substances, the calcium sulphide being set free, a similar action taking place with the carbonic acid in contact with the air. The bleaching of the mass on exposure to the air is due to the oxidation of the black iron sulphide to iron sulphate, which is removed by washing. The decomposition of the felspar constituents may also ensue from the long-continued action of the water. According to E. von Sommaruga, of Vienna, the existing sulphates are decomposed by the air into sulphuretted hydrogen and carbonates, and these being removed with the water, the refractory nature of the clay is improved.

The Moulding.—The kneading and rotting accomplished, the porcelain mass is taken to another room to be moulded. This is effected either on a potter's wheel or in a mould.

The Potter's Wheel.—The potter's wheel consists of a vertical iron axis, on which a horizontal solid wheel is fixed, and caused to revolve by the feet or by steam-power, the motion in the latter case being regulated by the feet. A lump of clay is laid upon the wheel, the thumb being placed in the centre of the lump and pressed downwards; a hollow is thus formed, which is widened, or the walls continued vertically according to the shape of the vessel to be made. The constant revolution of the wheel easily allows the moulder to obtain a perfectly cylindrical form. By thus humouring the clay, elongating the vessel, again depressing it, widening it, and by continued manipulation in this manner, the most exquisite shapes are produced. To form the ridges or sharp edges of the vessel a small piece of iron, a strip of horn or wood, termed a bridge, is used. The perfectly formed vessel is cut away from the wheel by a piece of brass wire.

Moulding in Plaster of Paris Forms.—A mould is first taken from the pattern or original object, which may be of clay, wax, gypsum, or metal. The moulding is performed with dry material, with clay of the consistency of dough, or with fluid clay. The moulds must possess a certain amount of elasticity, and be porous in order to absorb the moisture expressed. For these reasons plaster of Paris is generally used. The mould is taken from the original article in parts, which are trimmed to fit together accurately; into each part is then pressed sufficient clay to fill the indentations of the pattern, more clay being added till a proper thickness is obtained. The parts are then fitted together, and the moulds left for some time. This method of moulding is sometimes called presswork, and is adapted to all kinds of pottery not of circular form. Plates, cups, and dishes are also made in a similar manner. A leaf of clay is rolled out and pressed between flat moulds. Sometimes, instead of rolling, the clay is beaten out with a wooden hammer covered with leather.

Casting.—Moulding porcelain articles out of thin pulpy clay is one of the most ingenious arts of the potter. The fluid clay is poured into porous moulds, which absorb a portion of the water, thereby reducing the pulp to a certain consistency. The interior pulp remaining fluid is now poured out, and the cast or coating of clay adhering to the mould allowed to harden. When sufficiently hard the vessel is taken to the lathe to be finished, or if not of circular form, to the finishing room, where with sharp tools any required pattern is cut, or handles, spouts, &c., which have been made in separate moulds, attached.

Preparation of Porcelain Articles without Moulds.—The finest porcelain is finished by hand, as machinery or moulds could not give sufficient sharpness to the beautiful flowers and figures sculptured on vases, &c. The flowers, &c., are first prepared in moulds, are then attached to the body of the article, and finally are finished off with edged tools. The stalks of the flowers are sometimes formed on wire; and the leaf in first roughly constructed in the palm of the hand, the furrowing and veining being done afterwards. The texture of drapery is imitated by means of a piece of tulle, which is laid on the clay, and allowed to dry. During the burning the tulle is consumed, leaving the pattern on the porcelain.

Drying the Porcelain.—After the porcelain ware is formed it is dried for some time at the ordinary temperature. This is continued till the clay contains no moisture, that is, until its weight is tolerably constant. During this drying the clay is said to be in the green state, and possesses a greater tenacity than it has in any of the former processes.

Glazing.—Only very few articles of porcelain ware, generally statues or figures, remain unglazed; these are termed *biscuit ware.* All other articles are glazed. The glazings employed are of four kinds:—(1) Earth or clay glazings are transparent, and formed by melted silica, alumina, and alkalies; they easily become fluid, and melt about the temperature at which the vessels are baked. This kind of glazing is used for hard porcelain. (2) Lead glazes are transparent glazes containing lead; most of these melt at the temperature at which the articles are burnt. (3) Enamel glazes are partly white, partly coloured opaque glasses containing tin oxide besides lead oxide. This kind of glaze is easily melted, and serves to cover the unequal colour of the under mass. (4) Lustres are mostly earth and alkali glazes. This class includes the ordinary salt-glazed ware, as well as glazes containing metallic oxides used to imitate gold and silver surfaces for ornament merely.

Porcelain Glaze.—We will here, however, concern ourselves only with porcelain glaze. It is necessary that this glaze should melt readily at the temperature at which the article is fired; that it should be colourless and opaque; that it should fire sufficiently hard to withstand pressure, grinding, and ordinary cutting. The glaze is added to the porcelain mass with a flux, so that the melting may be readily effected. At Meissen the glaze used contains—

Quartz	37·0
Kaolin from Seilitz	37·0
Lime from Pirna	17·5
Broken porcelain	8·5
	100·0

In the Berlin porcelain manufacture the following glaze is employed:—

Kaolin, from Morle, near Halle	31
Quartz-sand	43
Gypsum	14
Broken porcelain	12
	100

Applying the Glaze.—The glaze can be put on in four ways:—(1) By immersion. (2) By dusting. (3) By watering. (4) By volatilisation. The glaze is either mixed with the ingredients, or applied superficially by one of the preceding methods.

Immersion.—Glazing by immersion is employed in the case of porcelain, the finer fayence ware, and sometimes for stoneware. It requires some degree of porosity in order that the glazing paste may be absorbed. The glazing materials are mixed with water to form a thin pulp. The articles previous to their immersion are slightly baked to prevent the clay being softened and running fluid in contact with the water of the glaze. The articles are dipped into the glaze, which they readily absorb, a coating or thin layer of glaze remaining on their surface when they are removed from the bath. The glaze is removed from the bottom of the article immediately in contact with the substance on which it stands to prevent its sticking.

Dusting.—Glazing by dusting is a surface method, and only used for costly ware. The freshly formed and still damp ware is dusted with lead glaze or minium, a layer being left on the surface. The powders employed chiefly contain lead oxide, which combines with the silica and alumina of the clay mass during the firing to form a glaze. Recently finely pulverised zinc blende and Glauber's salt have been employed.

Watering.—Watering is a method of glazing employed for non-porous articles, such as English porcelain, ordinary pottery ware, and some kinds of fayence ware. Glaze of the proper consistence is poured over the articles, the interior sometimes being left covered with a white glaze, while the outside is again coated with a coloured glaze, as is seen in common brown-ware.

By Volatilisation or Smearing.—Glazing by volatilisation is effected by conveying into the oven a salt or metallic vapour which shall form with the silica of the mass an efficient glaze. The most general method is applied to ware not requiring to be baked in fire-clay vessels. Common salt is placed in the oven with green wood for fuel to form an aqueous smoke. This, the salt, heated to redness, receives, and is decomposed into hydrochloric acid and soda, the vapours of which fill the oven. The inside and the outside of the vessel submitted to this process are thus simultaneously glazed. Fine stoneware baked in fire-clay vessels may be glazed by the ignition of a mixture of potash, plumbago, and common salt. During the baking or firing lead chloride is formed, which combines with the silica of the clay to form a thin glass. This method of glazing is in England termed *salting*, boric acid being employed.

Lustres and Flowing Colours.—A method of glazing by volatilisation, known as glazing with flowing colours, is employed for porcelain. It essentially consists in the ignition of a mixture of calcium chloride, lead chloride, and clay, placed in a small vessel in the firing capsule or firing chamber, and to which some metallic oxide is added, as cobalt oxide. The oxide is converted into chloride, and combines with the constituents of the article.

The Capsule, or Sagger.—Porcelain ware and superfine earthenware are not exposed, while burning, to the free action of the flame, as various impurities, such as ashes and smoke, would deteriorate the beauty. They are therefore enclosed in fire-clay vessels, termed in France *gazettes*, in Germany *kapseln*, and in England *saggers*. These saggers are manufactured of the best fire-clay, with which is mixed a cement made from broken saggers. First into each sagger is put a perfectly true disc of the same material, and upon this the porcelain ware is placed, three knobs or small props projecting from the disc, and keeping the article from contact with a large surface to which the glaze would cause it to adhere.

The Porcelain Kiln.—Fig. 434 is a vertical section of the porcelain kiln, Fig. 435 the elevation. The kiln is essentially a reverberatory furnace with three stages and five fire-rooms supplied with wood fires. The kiln may be considered as a tall cylinder, surmounted by a cone, in the apex of which is the chimney opening, the flat vaults by

which it is divided being pierced to allow of communication. Both the stages *L* and *L'* serve for the "strong firing" of porcelain. The upper stage, *L''*, termed variously the *howell*, *crown*, or *cowl*, serves for the "raw burning." At the bottom of both the lower stages are built the fire-places, *f*, leading by *g* into the kiln. *G* is the ash-pit, *T* the opening to the ash-pit closed during the burning; *o* is an opening through which fuel is introduced; *c c* are the openings, admitting of the circulation of the hot gases. *P* is

Fig. 434.

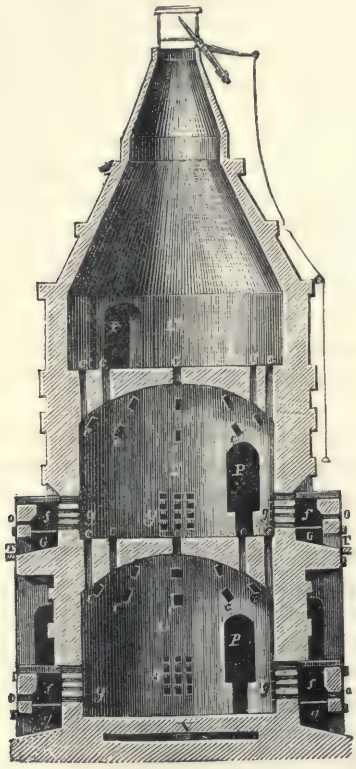
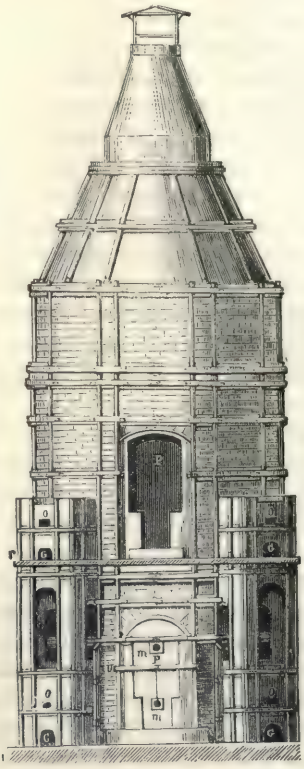


Fig. 435.



the door by which the kiln is entered. The kilns are gradually heated first to a glowing heat and then to a strong red heat. At this stage the openings are closed, and the kiln raised to a stronger heat, at which it is allowed to remain for a short time. This intense burning lasts about seventeen to eighteen hours; the kiln is then opened, and allowed to cool gradually for from three to four days.

Emptying the Kiln and Sorting the Ware.—After the kiln is cooled, the saggers containing the ware are removed, and the ware taken out. It is then separated into four kinds:—(*a*) Superfine, containing no blemish ware; (*b*) Medium, the ware slightly inferior in glaze, &c.; (*c*) The chipped and imperfectly glazed ware; (*d*) Waste, or ware so distorted or cracked as to be useless.

Faulty Ware.—The chief faults are:—Cracking from the porcelain not being sufficiently plastic, from drying unequally, and from unequal heating. Partial fusing from a too strong heat. Air-bubbles causing lumps to appear on the surface of the ware through the expansion of the air by heat. Spotting, from fragments of the sagger fusing and falling in upon the ware. Yellow-colouring, from smoke having entered the sagger. The chief faults in the glaze are:—Blowing, the result of the development of gas by the reaction of the constituents of the glaze upon each other; also resulting from too strong a firing. Shelling, or the exfoliating of the glaze.

Porcelain Painting.—Porcelain painting is really a branch of glass painting, the colours being glass colours, which when burnt in become durable and bright. The colours employed, technically termed muffle colours, are—

Iron oxide, for red, brown, violet, yellow, and sepia.
Chromium oxide, for green.
Cobalt oxide and potassium-cobalt-nitrite, for blue and black.
Uranium oxide, for orange and black.
Manganese oxide, for violet, brown, and black.
Iridium oxide, for black.
Titanium oxide, for yellow.
Antimony oxide, for yellow.
Copper oxide (and cuprous oxide), for green and red.
Iron chromate, for brown.
Lead „ for yellow.
Barium „ for yellow.
Silver chloride, for red.
Platinum „ for platinising.
Purple of Cassius, for purple and rose-red.

These colours are mixed with a fluxing material, so that by the melting a silicate or borate may be formed, yielding a good glaze. Therefore the cobalt oxide and the copper oxide must first be mixed with silicic acid and boric acid, oxide of antimony with lead oxide, &c., to form a blue, green, or yellow colour, because there are few metallic oxides yielding these colours that are not affected injuriously by heat or are by themselves sufficiently easily fluid. The burning in of the colours is effected in a muffle, Fig. 436, the opening *o* serving as a communnication with the interior, by which the degree of heat may be ascertained; the opening *m* serves for the escape of the vapours of the essential oils (oil of turpentine, oil of lavender, &c.), with which the enamel colours are sometimes ground up. Fig. 437 shows the method of heating the muffle. The heating is commenced at a low temperature and is gradually increased to a red heat. From time to time the muffle is opened till the colours begin to disappear; then the muffle is carefully closed, raised to a bright red heat, and finally allowed to cool as slowly as possible.

Fig. 436.

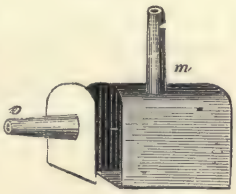
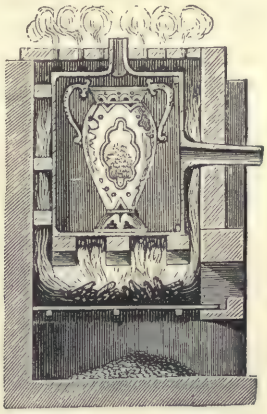


Fig. 437.



Ornamenting the Porcelain.—The gold employed for decorating the porcelain is dissolved in aqua regia, and precipitated with either iron sulphate, bismuth nitrate, or by means of oxalic acid. In its application the gold must be intimately mixed with a flux, generally mercurous nitrate. Shell gold is employed, also gold-beaters' refuse. The article to be gilt must be thoroughly freed from grease, else the gold will not adhere. The gold powder, finely ground up with sugar or honey, or some such soluble substance, is applied with a pencil brush. The burning in is effected in a muffle. The gold is not melted during the burning, but becomes firmly set upon the article by means of the flux. After burning the gold does not at once appear bright, but requires burnishing with an agate tool.

Bright Gilding.—Bright gilding differs from the foregoing in requiring no after

polishing or burnishing. It is effected by burning in a mixture of gold sulphide or fulminating gold in balsam of sulphur. When an article is gilded with precipitated metallic gold or a bright gold preparation, the gilding is secure from injury by handling or scratching with the finger-nail, &c.

Silvering and Platinising.—Silvering and platinising are usually only in slight requisition. Metallic silver is thrown down from its solution by means of copper or zinc; the platinum is precipitated from its neutral chloride by means of boiling with potash and sugar. The tarnishing of silver on porcelain by sulphuretted hydrogen may, according to Rousseau, be prevented by placing, before burning, a thin layer of gold upon the part silvered; the result then is a white layer of gold-silver. The silver and platinum are mixed with basic bismuth nitrate, painted on and burnt in, and afterwards burnished.

Lithophanie.—Transparent porcelain is used in the art of lithophanie, or making transparencies. A thin and unglazed porcelain plate is pressed into a flat gypsum mould bearing the pattern in high relief. The figures by transmitted light appear in delicately rounded tones of light and shade. The applications of this art to the manufacture of lamp shades, window ornaments, &c., are too well known to need remark here.

Very similar to lithophanies are the articles of porcelain and fayence now produced under the names *Email ombrant*, or *Email de Rubelles*, or lithoponies. They are, however, as regards the pressing, the very opposite to lithophanies, since in *Email ombrant* the darkest parts must be most depressed and therefore the thinnest, and the picture is seen not by transmitted but by reflected light. In these objects depressions are produced by means of moulds, and are then filled up with a semi-transparent and coloured mass of glaze, when the deepest parts take up thicker strata of glazing, and appear darker than the more elevated parts.

II. Tender Porcelain.—*French Fritte Porcelain.*—Tender or fritte porcelain is distinguished in commerce as of two manufactures, French and English. The French manufacture, in 1695, was first carried on at St. Cloud, near Paris, by Morin, who employed a glassy mass, without the addition of kaolin, but containing lead, somewhat similar to crystal glass. It can, therefore, hardly be considered a porcelain, strictly so called, until melted with lime and alumina. Thus *fritte* porcelain is composed of—(1) A glass mass or *fritte*, obtained from silica and alkalies. (2) Marl, as a clay constituent; chalk, as a lime constituent. The proportions of these constituents are—

Fritte	75	...	75
Marl	17	...	8
Chalk	8	...	17

The fritte is mixed with the chalk and marl to form a thin pulp, which is allowed to remain for a month to dry, and then again pulverised. When required quickly, plasticity is obtained by adding soap- or lime-water. Fritte porcelain is burnt in saggers, generally before glazing. During the burning this kind of porcelain softens more than the hard, and requires supporting on every side. It is for this reason generally baked in fire-clay moulds. The ordinary oven is employed. The glaze for tender porcelain is a kind of crystal glass containing lead. This glaze is poured over the articles, as they are non-absorbent on immersion. French porcelain is similar to cryolite glass or *hot-cast porcelain*.

English Fritte Porcelain.—English tender porcelain consists of a plastic clay, so-called *china clay* or *Cornish stone*, a weathered pegmatite, with fire-clay and bone-ash. The addition of the latter is due to Mr. Spade, in 1802; recently calcium phosphate, as apatite, phosphorite, staffelite, or sombrerite, has been substituted. The glaze is composed of Cornish stone, chalk, fire-brick, borax, and lead oxide. The article must be baked before glazing, as the glaze is so much more easily fusible than

the body of the article; and in this second firing lies the difference between the manufacture of tender and of hard porcelain. In hard porcelain the melting-point of the glaze and the body are the same. English porcelain is far less solid and more liable to crack than the hard; upon the other hand, English porcelain is the more plastic, and can be produced at a lower temperature in saggers of inferior fire-resisting qualities, consequently at a less expense. The burning takes place in a stage oven with anthracite coals, the articles being placed in saggers. The glaze is applied by immersion. Recently boric acid has been largely employed in glazing English porcelain.

Parian and Carrara.—Parian is an unglazed statue-porcelain, similar to English porcelain, but more difficultly fusible, containing less flux and more silica. The colour is a very slight yellow; the surface is wax-like. Parian was first prepared by Copeland, in 1848, although the idea was not new, as before this time Kühn, of Meissen, had prepared statues and medallions of porcelain in imitation of marble. The composition of Parian is very variable; some on being tested yield calcium phosphate, others barium silicate, and again some contain only kaolin and felspar.

Carrara, so named in imitation of the marble produced from Carrara in Tuscany, is intermediate to Parian and stoneware, is less transparent than Parian, and sometimes whiter in colour.

III. Stoneware.—Stoneware differs entirely from porcelain. It is dense, sonorous, fine-grained; does not cling to the tongue; it is semi-fused and opaque. Even fine white stoneware is different from porcelain in transparency, being entirely opaque, although in some other respects similar. Stoneware is distinguished—

1. As porcelain glazed.
2. As white or coloured unglazed.
3. As common stoneware, salt-glazed.

The fine white stoneware is made from a plastic clay, burning white, and not very refractory. To the clay is added kaolin and fire-clay with a felspar mineral, generally Cornish stone, as a flux. The glaze contains lead oxide and borax, and is transparent. The flux is used, in the making of stoneware, much more freely than in porcelain, in the proportion of more than half the weight of the mass. It follows that stoneware can be burnt at a lower temperature than porcelain. The articles are fashioned out of the plastic clay in the same manner as porcelain. Fine stoneware is used as a cheap substitute for porcelain, it being much more easily burnt.

White or coloured unglazed stoneware, or Wedgwood ware, is made from a plastic slightly refractory clay, kaolin, fire-clay, and Cornish stone, the latter in the proportion of half the weight of the whole. It is more easily fusible than porcelain, requiring a lower temperature in burning. The coloured stoneware is of the same composition as the white, the colouring being only superficial. Frequently other coloured clays are used for ornaments in relief. Coloured Wedgwood ware is known as Egyptian, bamboo, fine salt ware, fine biscuit, &c.

Common stoneware differs from the preceding in containing no flux, the clay being semi-fused by the continued action of the fire. To the clay is added fine sand, or pulverised fragments of stoneware. Chemical and pharmaceutical utensils, acid tanks, &c., are made of this ware, it being strong and durable. The colour is generally grey.

Stoneware Ovens.—The ovens for burning stoneware are so constructed that the articles can either lie down or be placed vertically. Fig. 438 is the vertical section of such an oven through the line *AB* in Fig. 439. Fig. 440 is a section through the line *CD* seen from *B*. Fig. 441 is a section through *CD* seen from *A*. Fig. 439 is the plan on the line *EF*, Fig. 438. *a a* is the arch or vault of the oven, built of clay; *b*, the vessel-chamber; *c*, the fire-room; *d*, the fire-bars; *e*, the stoke-hole; *f*,

the ash-pit; *g*, an air-draught; *i i*, a pierced wall; *k*, a pierced back-wall, through which the flame and hot gases escape into *o*, serving as a flue. Anthracite is used as

Fig. 438

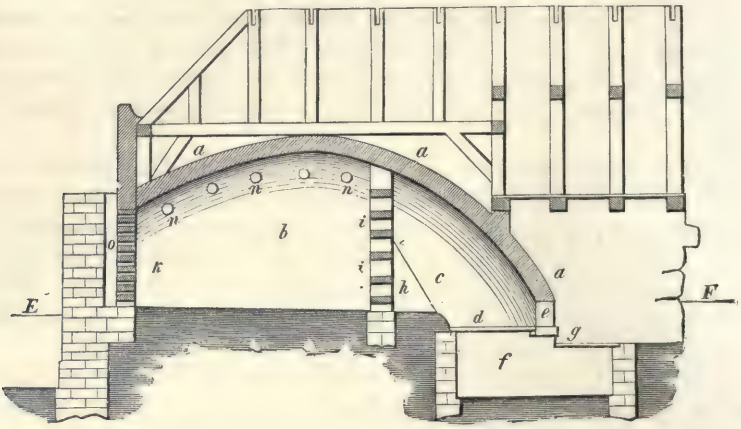


Fig. 439.

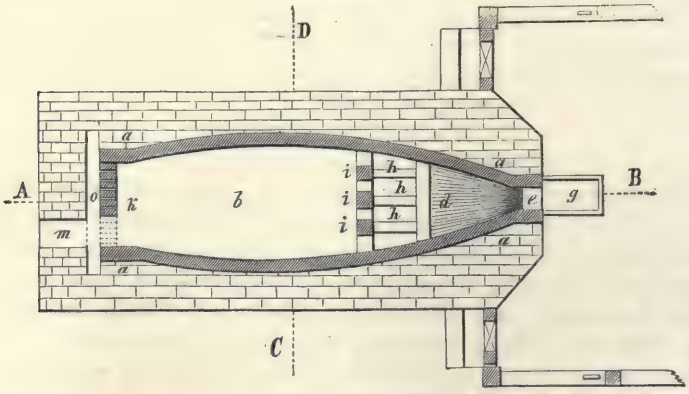


Fig. 440.

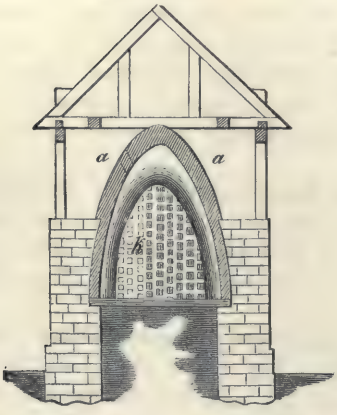
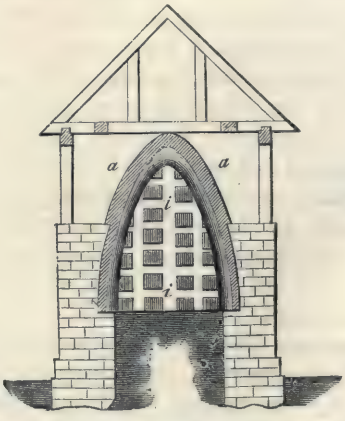


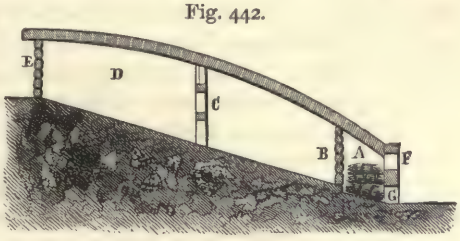
Fig. 441.



fuel. Another form of oven in which mineral-water bottles are burnt is shown in Fig. 442. It is constructed on an easy slope; at the lowest part is the fire-room, *A*. In the middle of the burning-room is the pierced wall, *C*, technically termed the

window, through which the hot gases and flame escape into *D*. The vault and walls, *B* and *E*, are of broken earthenware, bound with mortar. A chimney is unnecessary, the gases escaping through the pierced wall, *E*, into the air. The burning usually takes about eight days. The high temperature at which common stoneware is burnt, and the nature of its components, render glazing unnecessary; but generally a glaze is obtained with the help of common salt placed in the oven during burning. After the placing of the salt the openings of the oven are closed for some time, and then a second quantity of salt is introduced. The silica, with the assistance of the steam, decomposes the salt into hydrochloric acid and soda, with which it combines. Thus there is formed on the surface of the ware a glaze of sodium and aluminium silicate. The salt will take up more than 50 per cent. silica, according to Leykauf's experiments; therefore, the more silica the better glaze. An oven of moderate size will require 80 to 100 lbs. of salt; the purity of the salt is not a subject of much consideration. The glaze is colourless, and the vessel appears the colour of the clay. Stoneware that is unequally coloured, one part brown, the other grey, has been brought to that state by escape of hydrocarbons into the burning-room.

Fig. 442.



Lacquered Ware.— Lacquered ware, known as Terralite and Siderolite ware, is manufactured in Northern Bohemia by the firm of Villeroy & Boch, of Mettlach, and is an intermediate ware to fine and common stoneware. It has no glaze, but a strong surface colour of varnish or lacquer. Candlesticks, bowls, flower-vases, jugs, flower-pots, baskets, butter-dishes, fruit-dishes, &c., are formed from this ware, and baked in saggers in the usual manner. Great care and attention are required in burning the ware. The colour or bronze is mixed with varnish, thinned with turpentine or linseed-oil, and applied with a pencil. The ware is then placed in a slow oven; the ethereal oils volatilise, and the bronze colour becomes fixed to the surface of the ware.

IV. Fayence.—Fayence ware (English fine stoneware) derives its name from the town of Faenza, in Central Italy, where the ware was skilfully made. In the ninth century the Spanish Moors manufactured fayence in the Island of Majorca, whence the present majolica, the slight alteration in the manner of spelling being accounted for by Dante, in his "*Tra isola di Capri e Majolica*," on the ground that the older Tuscan writers spell the name of the island "Majolica." The industry developed from the thirteenth to the fifteenth century; from that to the seventeenth it culminated, and then commenced to decline. In the middle of the sixteenth century Bernard Palissy introduced the ware known as Palissy-fayence into France. Palissy's celebrated *pièces rustiques* consist of ware ornamented with fish, fruit, vegetables, &c., naturally coloured in enamel. The body of porous fayence ware is earthy, and clings to the tongue. It is opaque, with more or less plasticity, and little or no sonorosity. It consists generally of plastic clay, or a mixture of this with common potter's clay. It differs from clay ware in the employment of finer material, manipulated with greater care. Fine white fayence is distinct from common enamelled fayence. Fine fayence (semi-porcelain) consists of a plastic clay with pulverised quartz or fire-bricks, with kaolin or pegmatite and felspar minerals. It remains white after burning, and is coated with a transparent glaze. The fayence wares of different countries differ greatly; some are easily fusible, others again are burnt at a high temperature. The composition of the glaze is therefore very varied. Common lime fayence is a mixure of potter's or plastic clay, marl (clay with calcium carbonate), or quartz and quartz-sand. It is characterised by containing 15 to 25 per cent. of

lime, which, at the low temperature at which common fayence is burnt, only loses a portion of its carbonic acid. The common fayence ware is thus easily distinguished from other wares by its property of effervescing when an acid is poured into a vessel made of this ware. Its fracture is earthy; the colour, consequent upon its containing 2 to 4 per cent. of iron oxide, is a decided yellow, so that an opaque glaze is employed. The glaze or enamel contains usually tin and lead oxides, alkalies, and quartz. The more iron oxide and lime contained in the mass, the lower the temperature required for burning. Fayence, like porcelain, is twice burnt, first without, and secondly with, the glaze. It is burnt in saggers; the ware is placed in the saggers, and these are piled one upon the other in the furnace, with a layer of fat clay between each pair The articles stand in the saggers upon small tripods, in order to expose as small a contact surface as possible. The hard-burnt ware has next to be glazed. A thin pulp with water is made of the materials of the glaze placed in a cistern into which the articles are dipped. The glaze usually consists of felspar (Cornish stone), fire-clay, heavy spar, sand, borax and boric acid, crystal glass, soda and sodium nitrate, white-lead, minium, and smalt. The composition of this glaze is ordinarily very complicated, but the essential constituents are silica, boric acid, alumina, lead oxide, and alkali. Recently the Peruvian mineral, so-called *tiza* (sodium and calcium borate), has been employed. The addition of lead serves to render the glaze easily fusible, while the felspar imparts the softness characteristic of a lead-alkali glaze.

Ornamenting Fayence.—Fayence is ornamented by—1. Painting; 2. Casting; 3. Printing; 4. Lustring. Painting is usually done with the brush, partly under, and partly upon, the glaze. The glazing oven not attaining so high a temperature as the porcelain oven, the colours are not affected by the heat. The colours used are chromium, cobalt, iron, antimony oxides, &c. The rose- and purple-red colours are obtained from gold preparations. The pink colour, carnation pink, was discovered in this country, and is a stannic chromate. To make this colour—

Stannic acid	100
Chalk	34
Potassium chromate	3–4
Silica	5
Alumina	1

are well mixed and allowed to stand for some hours in a strong heat. The mass appears as a dirty rose-red colour, attaining its full brilliancy when washed with water acidulated with hydrochloric acid. The casting consists in the fayence vessel receiving a surface layer of coloured clay in any required part, independently of the colours of the mass. These coloured clays or clay-washes are made of the ordinary fat clays d metallic oxides. The printing is accomplished with the aid of thin tissue-paper, upon which the pattern is first printed from a copper plate, and afterwards transferred to the ware. For black, a mixture of forge-scale, manganese, and cobalt oxide or chrome-black is employed; for blue, cobalt oxide mixed with, for bright blue, fire-brick, and for less intense colours, heavy-spar, both of course being pulverised. This mixture is burnt, the frit ground, and mixed with a flux of equal parts of flint-glass and fire-clay. Copper plates, in which the pattern is deeply cut, are charged with colour mixed with linseed-oil; a transfer is then taken on the fine "pottery tissue" paper, and laid on the ware. By means of a rubber the colour is caused to leave the paper, which has been previously moistened with water, and adhere to the ware. The paper is then washed off, and the article taken to the kiln.

Flowing Colours.—Flowing colours are much employed in ornamenting fayence. The common fayence or delft ware is coloured blue in this manner by means of cobalt oxide mixed with the glaze. When the vessels are taken to the burning-kiln, a

mixture of calcium chloride, lead chloride, and clay is also introduced on a small plate. The cobalt oxide is converted into a chloride by combining with the volatilised materials, and in turn combines with components of the material of the vessel. By this means the articles obtain an apparent transparency somewhat similar to that characteristic of porcelain.

Lustres.—Some kinds of ware have a second coating—a metallic lustre or glaze—given to them after burning. Gold Lustre: The different kinds of gold lustre are very similar and need not be detailed. They are essentially composed of fulminating gold and balsam of sulphur, the latter prepared by heating linseed-oil and sulphur together. Platinum Lustre: This is obtained by mixing anhydrous platinum chloride with lavender-oil or balsam of sulphur; also by the well-known precipitation of platinum with sal-ammoniac. Silver Lustre is either a yellow lustre or a cantharidine lustre, so called from its similarity in appearance to the wing-cases of the Spanish fly (*Cantharis vesicatoria*). Salvétat believes that silver chloride may be employed as a yellow lustre, similarly to gold preparations. The cantharidine lustre is generally a yellow lustre, the difference being that it is only used for white grounds, while the former is employed for blue grounds, on which it appears slightly tinged with green. Copper lustre is both red and yellow; it is used for Spanish fayence and majolica wares. It is chiefly formed by a copper silicate. Lead oxide, or lead lustre, is merely a lead glaze. Silver chloride, mixed with lead lustre, is reduced, the result being a deposit of a gold-yellow or a silver-white colour, according to the proportion of silver.

Etruscan Vases.—The vases of the old Romans were a kind of fayence ware, containing iron, and formed of a clay decomposed by quartz, only slightly burnt, sometimes unglazed, sometimes coated with an easily fusible glaze. These vases and articles are celebrated more for their beauty of form than for any peculiarity in composition, which is very analogous to the well-known delf ware of which our table-services are made.

Clay Pipes.—In the manufacture of clay pipes there is employed the beautifully white pipe-clay, containing neither iron, nor sand, nor carbonate of lime. The clay, if pure, always burns white; but occasionally, when a yellow colour appears, the clay is burned for a longer time, whereby the iron oxide colouring the clay is removed. The pipes are formed in a mould similar in shape to the pipe. A roll of clay is taken, and carefully spread out to the length of the pipe. The mould is constructed in two parts, hinged together like a meerschaum pipe-case, and is generally of iron. The roll of clay is placed on the lower half of the mould, and the upper half is then pressed or screwed down. A wire is then pushed up the entire length of the stem. The pipe is then taken out of the mould, and set aside to dry. It is afterwards taken to the oven, where about a gross of pipes are introduced into each sagger. The saggers are long clay tubes. Sometimes the pipes are burnt without saggers. To prevent the pipe adhering to the lips on account of the porosity of the clay, the end put to the mouth is rubbed with a mixture of soap, wax, and lime-water.

Water Coolers.—The Spanish water-cooling vessels, or *alcarrazas*, are made of a porous, unglazed earthenware. The constant evaporation of the water exuding to the outer surface of the vessel causes the water to be kept cool in the hottest climates. The vessels are only slightly burnt. According to Sallior, water can be cooled 15° in an alcarraza, while Sèvres ware only permits of the cooling of its contents in a similar manner some 2° or 3°. These vessels are known in France as *hydrocérames*. In this country Egyptian wine and butter coolers are very common, while in Egypt, Spain, Turkey, the Indies, and Americas they are really necessaries. In Bengal these coolers are made from the mud of the Ganges. In the Levant they are termed *baldaques*; in Syria and Egypt *collies* or *gullies*, while in many places they are also known as *gargoulettes*.

V. Common Pottery.—To distinguish between the different kinds of this ware is extremely difficult. The manufacture is entirely distinct from the preceding. For the so-called white pottery, used for culinary purposes, ordinary potter's clay is employed, and for brown ware a moderately refractory clay. The natural clays are, as a rule, too fat to be used without the addition of some other material, generally sand; besides sand, fire-brick, chalk, charmotte, and anthracite coal-ash are employed. The vessels are formed upon a potter's wheel, air-dried, and then glazed. The employment of a lead glaze was but a short time ago unknown in the glazing of this kind of ware. Ordinarily the mass is white or yellow, sometimes brown-red; the glaze being transparent, the colour of the body or mass is always visible. Partly because the ware is very easily fusible, and partly because a low heat is used in the burning, the glaze must also be very easily fusible. For this reason a lead glaze, forming an aluminium and lead glass is very applicable, and is employed mixed with loam (clay and sand). The materials are ground and very intimately mixed in a hand-mill. The lead used is generally a lead-glance. During the burning the lead-glance is roasted, and the sulphur is driven off as sulphurous acid. The lead oxide combines with the silica and alumina of the loam, or mixture of sand and clay, to form aluminium and lead silicate.

The glazing of the air-dried ware can be performed in three ways: either by immersion, by sprinkling, or by dusting. By immersion the workman's hands come into contact with the lead-containing glaze, with detriment both to his health and the adhering of the glaze if his hands should be greasy. This method is not therefore often employed. Sprinkling is generally adopted. In dusting, the ware is first immersed in a pulp of fat clay, and then, while still damp, dusted with the finely pulverised glaze. The danger of this process is the inhaling of the fine particles of glaze floating in the air of the work-room. When the lead oxide is properly proportioned to the silica of the clay or loam, the resulting lead-glass is not affected by ordinary organic acids. But if the lead oxide is not well combined with the silica, it will be dissolved by boiling vinegar. The experiments of Buchner, A. Vogel, Erlenmeyer, and others have shown that the insolubility of lead-glaze is not so great as has been supposed, very dilute vinegar in some cases being sufficient to effect a solution. The use of vessels thus glazed may therefore have no little influence upon the health of a family, and it becomes necessary to consider if there is not some substitute. All injury likely to accrue from the use of this glaze would be removed if the potter would but reburn imperfect ware, or employ ovens of the best construction; but this is not always the case. Recently the preparation of a glaze free from lead has been attempted, by employing water-glass, or a mixture therewith of calcium borate.

Burning.—The glazed vessels are next taken to the oven. This is generally a reverberatory furnace, $2\frac{1}{4}$ to $2\frac{3}{4}$ metres in height, and 7 to 10 metres in length. At one end is the fire-grate, and at the other the chimney. The vessels are burnt without saggers, and are exposed to the full influence of the flame. The fire is at first kept low for eleven to twelve hours, and then maintained strongly for four to five hours. The vessels can be removed from the oven about eighteen to twenty-four hours after being burnt.

VI. Brick and Tile Making.—The bricks of modern times are very distinct from the unburnt, air-dried clay lumps; although these are still in use in some districts.

Terra-cotta.—The term terra-cotta ware generally includes the burnt, unglazed yellow or red clay ware, and also tiles, employed in building and architectural ornamentation. The preparation of this ware is almost entirely mechanical, and does not call for any further elucidation in this work than will be found in the following pages descriptive of the class of manufacture to which it belongs.

Brick Material.—Various clays are used in brick-making. Usually those only are selected that will form a brick capable of bearing a considerable strain. In the burning a test-brick is employed, which is removed from time to time to see the progress of the fire, to prevent the over-burning of the bricks, or the lowering of the fire till the bricks are sufficiently burnt; but this brick must not be confounded with another test-brick for the following purpose. A brick is made of any new clay to be tested, and is set apart in an active kiln, being burnt at the same temperature as the bricks of this kiln afterwards sent into the trade. By the qualities of this test-brick the nature and worth of the new clay is judged. A batch of bricks should be composed of clays that may all be burnt at the same temperature, else very unequal results will follow; some bricks will be under-burnt and some over-burnt, while only those bricks to the clay of which the temperature is adapted will be of use commercially. A brick-clay containing much calcium carbonate can be burnt at a very low temperature, and indeed bricks so composed are very solid, and have great durability. Brick-clays often contain felspar, mica, ferric hydrate, and phosphate, besides organic matter. When these are not in large quantities their presence is not detrimental. Mica and felspar with iron oxide act as fluxes, and in moderate quantities are useful rather than pernicious. Flint stones, large pieces of calcium carbonate and gypsum, interfere with the easy utilisation of brick-clays. Sulphur pyrites render clays unsuited to the manufacture of bricks, as the iron sulphide remaining in the brick after burning oxidises in the air to sulphate, which in a short time weathers out and renders the brick brittle. In the Netherlands, in the Thames near London, on the banks of the Ganges and Nile, in the muds of rivers, and in nearly all clays exposed to the ebb and flow of water, is found an admirable material for brick-making. Since 1852 a mixture of lime, river-sand, and water has been extensively used as a brick material, and for other building purposes.

Preparation of the Clays.—The excavating of the clay for making bricks is carried on in the summer or spring. The clay is placed in not too high a layer, and allowed to weather. It is very advantageous if, during the weathering, a frost sets in. The clay is allowed to remain thus exposed to atmospheric influence until it becomes boggy or marshy. In this condition it is brought to a tank dug in the ground, 4 metres long, 2 metres broad, and 1·3 metre in depth, where it is mixed with about as much water as will stand to a height of 6 centimetres in the tank. So soon as the clay is thoroughly saturated it is treadled—that is, the brick-maker fastens boards or wooden shoes to his feet, and carefully treads over the clay, picking out all the flints, &c., which resist the passage of his foot to the bottom of the layer. This process is repeated two or three times. Sand is then added to the clay. If the clay is fat the mixture is proceeded with; but if it is a poor clay it is advantageous to wash out a portion of the sand. This may be effected in two ways. The ground-tank just described may be flooded with water, and the sand allowed to settle to the bottom; or the mixed sand and clay is placed in a large wooden tub, with a hole in the side near the bottom stopped with a plug. When the water has thoroughly impregnated the clay it is let off, carrying part of the sand with it. Or the clay is stirred with the water to a thin pulp, and allowed to run out of the wooden cistern into a ground-tank, where, with the water, the sand settles to the bottom. London clay, being mostly alluvial, has to be very carefully treated to free it from flint stones, &c.; it is afterwards mixed with ash or sand.

The "treading" of the clay is at the present time performed in mills, termed "pug" mills and "washers." At the International Exhibition (1871) several machines were exhibited for performing the whole process of brick-making continuously. Among these was the three-process brick-making machine of Messrs. Clayton, Son, & Howlett, of the Atlas Works, and combining at one operation crushing, pugging, and brick-

making. The rough clay is thrown into the hopper of the machine; in this hopper revolves a shaft, upon which are keyed several small knives to cut up the clay previously to its being crushed. It next passes through a pair of crushing rollers, and these effectually reduce any stones or hard lumps of clay which may enter. The clay, thus partially prepared, next passes into a horizontal pugging or mixing cylinder situated beneath, where it is mixed by the pug-knives fixed upon the central shaft. The knives force the clay towards the further end of the cylinder, where it is received by rollers and forced through the dies, forming a smooth bar of clay of the width and depth of a brick. This bar is cut into the required lengths by wires. The machine is capable of producing 20,000 to 30,000 bricks per diem, and is, perhaps, the best of its class. Mr. Rawden has constructed a machine in which no rollers or crushers are employed, the clay being turned out as wet and as soft as in hand-moulding. One horse-power will pug the clay and mould from 12,000 to 15,000 bricks per day. It consists of a square pug-mill, through which runs a vertical shaft bearing pug-knives. On the top of this shaft, above its bearing, is attached the horse-pole, which gives motion to the whole machine. Upon the lower end of the shaft, which passes through the bottom of the pug-mill, is a wheel having two cams, on which two rocking-arms work. One arm presses the soft clay through a grating into a six-brick sanded mould, and the other arm is connected to a slide for pushing the empty sanded moulds under the grate, the empty mould at the same time pushing the full one out. Among the best continental machines are those of Henschel of Cassel, and of Karrens.

The moulding of bricks and tiles is effected partly by hand, but chiefly by machinery. The burning is effected either in kilns or in specially constructed furnaces. They are either open or closed, or arranged for continuous work, and burn either wood, peat, lignite, coal, or gas.

The brick furnaces with unintermittent action are coming more into use. The first step in this direction was the furnace of Hoffmann and Licht. It consists of a circular channel, which is accessible from without in its various parts, and closed at as many parts, against a central chimney. Hoffmann's ring furnace is usually a smooth building, 3–4 metres in height, and flat above. The chimney rises generally in the middle of the masonry, but it may be placed externally. The whole is covered with a slight roof for protection against the weather. The furnace itself may be round, oval, oblong, three- or four-sided, or even of horse-shoe shape.

The space for burning is a vaulted continuous channel, returning into itself. This endless channel has in its top a number of openings, equally distributed, the heating-holes. There are also a number of doorways, which pass through the outer wall. In the inner and hinder wall of the burning space there are an equal number of smoke-flues. A movable partition, filling up the entire cross-section of the burning space, can be introduced into the endless channel, so that at its right hand in front there is always a doorway, and at its left, behind, a smoke-flue. Latterly, instead of this, iron slide-paper has been used, which is torn by means of a cord when the fire is to advance into a chamber. All the outer doors and flues can be closed so tightly that, if one of them is opened, the others may be considered as non-existent.

The smoke-flues open into the smoke-chamber, which is a connecting link between the burning space and the chimney, and may either lie on the horizontal plane of the burning-space by which it is surrounded and protected, or it can be placed below, above, or outside the furnace.

Of the following figures, 445 shows a vertical section; 446 in its upper half a view from above, and in its lower half the ground plan of a circular ring furnace, in which the movable partition is introduced from above through slits in the vault of the furnace; 443 is a small ground plan; 444 shows the manner in which the smoke-flues are closed air-tight. If we suppose the section of the furnace closed at one point by the intro-

duction of this movable partition; if we suppose this entrance doorway and the adjoining smoke-flue opened, but all the other entrance doorways of the outer wall and all the other smoke exits of the back wall are closed, the air passes through the open door into the burning spaces, traverses it through its entire length, as far as the other side of the movable partition, passes here through the open flue to the smoke-chamber, and thence to the chimney.

Fig. 443.

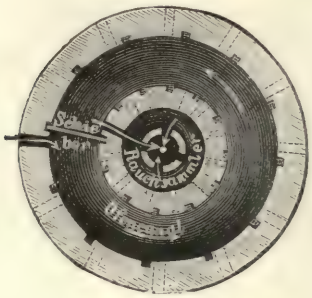


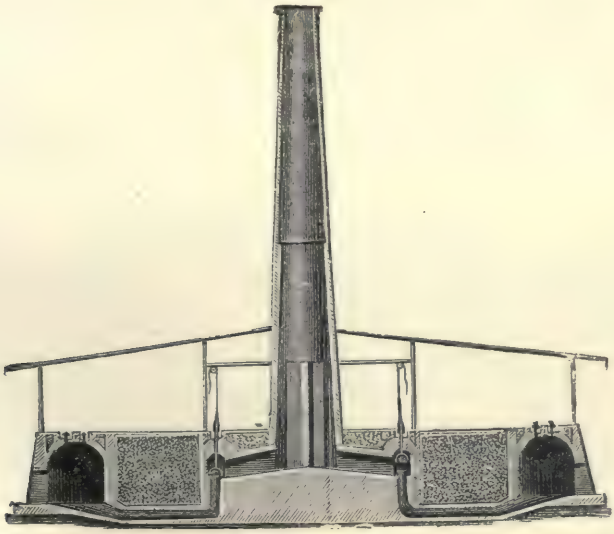
Fig. 444.



Explanation of Terms.

Schieber	Slide.	*Rauchsammler*	Smoke-collector.
Rauchsammler	Smoke-collector.	*Glocke*	Bell.
Ofencanal	Kiln-channel.	*Fuchs oder Rauchcanal*	Smoke-channel.

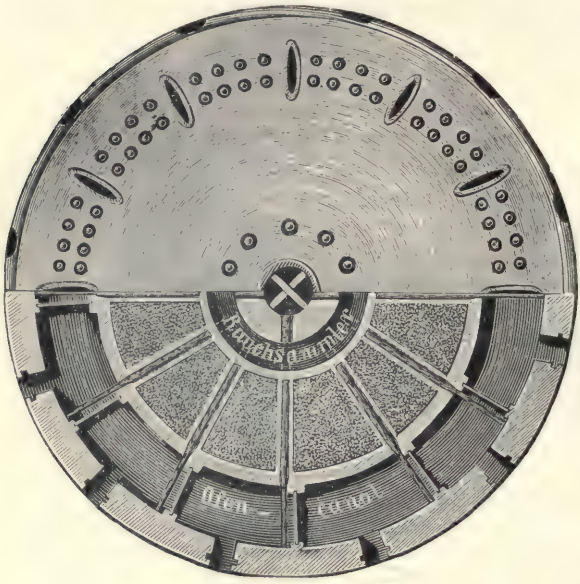
Fig. 445.



When the bricks which are nearest the open outer door are cooled down in such a manner that they are fit for removal, their place is taken by fresh, unburnt bricks. The closure of the furnace is then effected at the next door on the right hand, and behind the raw bricks which have just been put in. This door is then opened and the former one is closed; in like manner the next flue is opened and the former one closed, and the fire is advanced forwards by the length of the compartment. By continually repeating this process the fire makes the entire circuit of the furnace. Burnt bricks are simultaneously taken out and raw ones put in without interruption. If we pass

round the furnace, setting out from the movable partition in the opposite direction to the advancing combustion-gases, we have the furnace-channel on our right. We first pass bricks which have only just been put in and are therefore still cool; then to others which are gradually warmer and warmer, until in the middle of the circuit we meet the full fire. Beyond that point we meet with bricks which are still strongly heated and then successively with such as are cooler and cooler, and at the first open door we find such as are quite cold and are being carted away. At the next open doors the men are engaged in charging the furnace with raw (technically *green*) bricks.

Fig. 446.

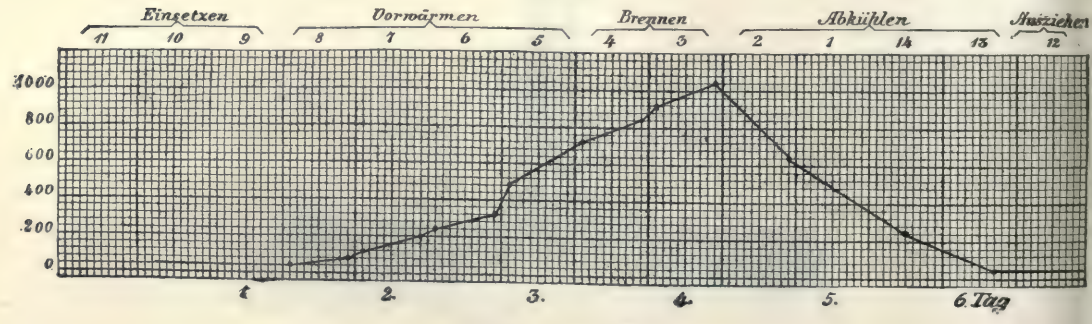


Explanation of Terms.

Rauchsammler	Smoke-collector.
Ofencanal	Kiln-channel.

According to the author's experiments the charge for the fourteen chambers of a ring furnace requires seven to eight days for thorough burning. The highest temperature was 1057°, whilst the gases escaped at 108° and 172°. The diagram, Fig. 447, shows the rise and fall of the temperature. The proportion of carbon dioxide in the gases taken at the bottom is essentially larger than under the vault, and carbon monoxide is found only when the gases are taken direct from the coals introduced. In

Fig. 447.



Explanation of Terms.

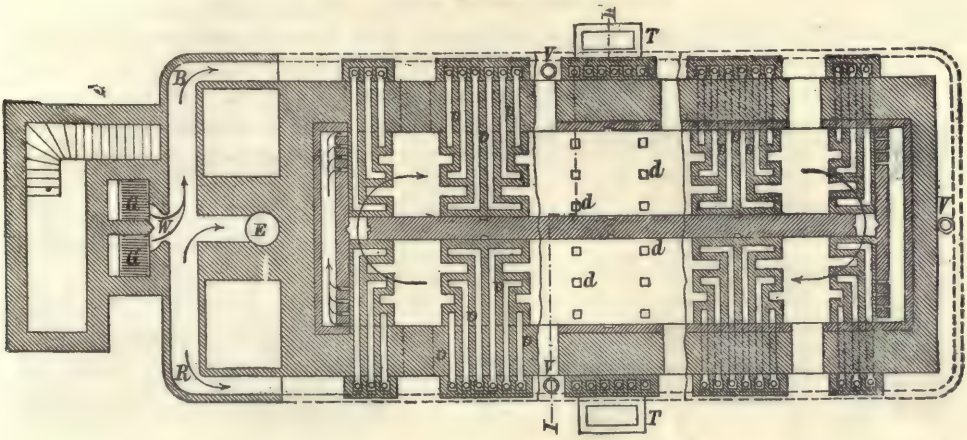
Einsetzen	Putting in.	*Abkühlen*	Cooling off.
Vorwärmen	Preliminary heating.	*Ausziehen*	Taking out.
Brennen	Burning.	*Tag*	Day.

ring-furnaces a reducing fire can scarcely occur even transiently, thus obviating the discoloration produced by sulphuretted coal. But, generally, facing-bricks of a good colour are more difficult to produce in ring-furnaces than in common furnaces. The quantity of coal consumed depends on the quality of the clay. From 242 to 360 bricks

take 1 cubic metre of furnace space. Ring-furnaces may be used for brick-making either on the small or the large scale.

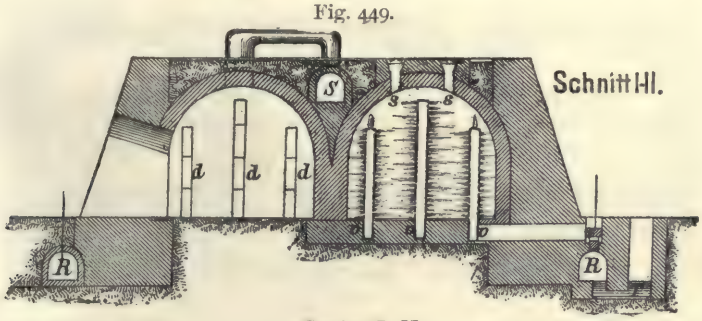
Bock has recently devised a channel furnace in which the green bricks, &c., are brought on trucks, meeting the furnace-gases up to the fire, where they are fully burnt, and as they pass onwards they give off their heat to the furnace-gases. The propulsion of the trucks often involves difficulties.

Fig. 448.



Gas-firing.—In Escherich's ring-furnace the gas produced in the generators, *G*, issues from the flues, *v*, into the pipes, *d*, built of hollow stones, and issues from numerous lateral openings 5 to 20 millimetres in width, where it forms flames of 3 to 20 centimetres in length, at right angles to the direction of the draught (Figs. 448 and 449). By this distribution of the gas the bricks themselves are not touched by the flame, and the composition of the gases in the entire cross-section of the burning channel is uniform, so that the production of pure colours is relatively easy. If a reducing flame is required the access of air is moderated by means of the smoke-valve.

Fig. 449.



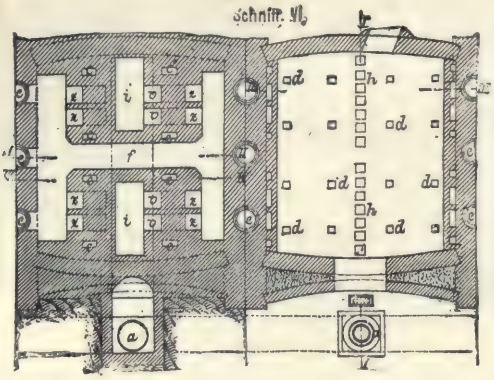
Section I.–II.

As the entrance of the gas and the exit of the smoke are remote from each other, it is possible to use the ring-channel simultaneously for gas and smoke, by connecting the alternating trap on the one hand with the generators, *G*, and on the other with the chimney, *E*. The tar deposited from the gas collects in the receivers, *T*. Numerous cross-channels, *v*, connect the ring-channel with the furnace-chambers. The burning channel is itself divided into four compartments by the three bells, *V*, the first of which is in direct connection with the chambers 1 to 4, the second with chambers 5 to 8, and the third with chambers 13 to 16. By raising and lowering the bells the

connections between 1 and 2, 1 and 3, 4 and 3, &c., can be opened or closed at pleasure. By a suitable placing of the alternating apparatus each division of the ring-channel can be connected either with the generator or the chimney. The same flues and bells which effect the introduction and distribution of the gas in the various chambers serve to carry off the smoke. Lastly must be mentioned the smoke flue, *S*, and the view-holes, *s*, introduced between every two rows of pipes.

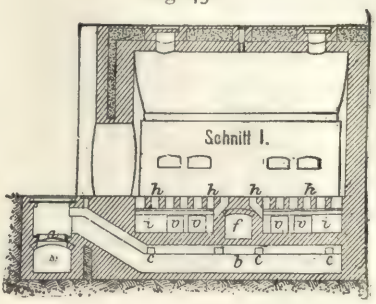
Mendheim, of Munich (German patent 22,086), effects a uniform distribution of temperature by causing the generator-gas of each chamber to enter the channel *b* through the valves (Figs. 450–452), *a*, and to pass from here by means of the branch

Fig. 450.



Section VI.

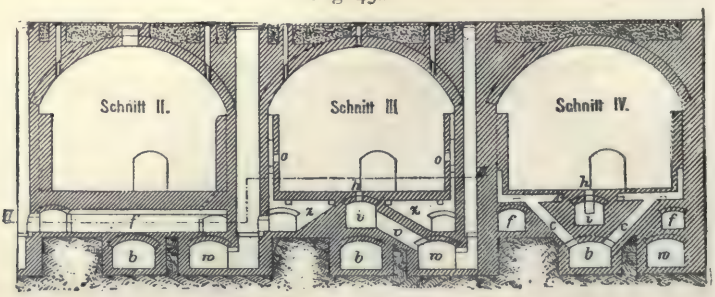
Fig. 451.



Section I.

flues *c*, underneath the sole of the furnace. Here a part of it passes through the openings *d*, into the space filled with bricks, after heated air has passed beneath the sole from the flues *z*, and has formed flame, which then streams from below upwards; another part of the gas arises behind the fire-bridges. Here the gas comes together with the hot air issuing from the flues *z*, in order to be conducted through the charge

Fig. 452.



Section II. Section III. Section IV.

from above downwards. The entire escape of the flame from the heated chamber takes place through the openings *h*, so that both the fire coming from the fire-bridges and that from the sole of the furnace pass unitedly through *h*, and the channels *i*, *v*, *w*, and the plate-valve, *e*, into the channel *f*, of the next chamber and its ramifications, *z*. This furnace is found to work well.

Kilns.—If peat or wood is used as fuel the bricks to be burnt are piled up in a heap much in the same manner as they would be placed in a furnace; several fire-flues are left in the mass, and the entire mound, which may contain 50,000 bricks, is covered with a thin coating of clay and protected on the windward side with movable screens

of straw. The fire is inserted in the flues which have been left; the gases sweep through the mass of bricks and escape at the top. If coal is used as fuel the flues are made narrower than for peat. Upon every layer of bricks is laid a stratum of small coal, then another layer of bricks, then more coal, &c. The kiln is covered with clay, in which air-holes are left to regulate the burning. The coal placed in the flues is kindled, and the fire gradually extends through the kiln.

Clinkers are bricks burnt until they are half vitrified.

Roofing-tiles.—For tiles a better clay is required than that for bricks, and it must be more carefully prepared. Tiles are generally burnt along with bricks, occupying the upper portion of the kilns. If it is desired to produce tiles of a grey cast, twigs of alder, with their leaves green and moist, are placed in the kiln at its greatest heat, and the air-holes are closed. The smoke thus produced deposits carbon in the porous tiles, and perhaps reduces part of the iron to the ferroso-ferric state.

Flooring-tiles.—The manufacture of flooring-tiles agrees mainly with that of roofing-tiles. They are four- or six-sided, and are used for paving kitchens, fore-courts, cellars, &c.*

Ballast consists of clay or arable soil not moulded into any definite forms, but lightly burnt in the state of irregular fragments. The fuel is partly coal of the worst sort obtainable, and partly the contents of the dust-bins, *i.e.*, a mixture of cinders with very promiscuous animal and vegetable matter. The smell given off is most disgusting, as the process is little more than a semi-destructive distillation. This ballast is used for making poor roads, garden walks, &c., and it is converted into an inferior sort of brick by grinding to powder, mixing with water, and moulding under powerful pressure. The use of such bricks is one cause of the very perishable character of the houses run up by building speculators.

An important point for determining the value of bricks, at least in extreme climates, is their resistance to frost. A clay gave at different temperatures:

Burnt at—	Porosity. Per cent.	Disruptive Force. Kilos. per square centimetre.
700°	11·23	16·5
800	10·56	22·4
850	10·22	25·2
900	9·53	30·5
960	8·16	44·2
1050	2·11	59·5

Some samples which had been burnt at 800° to 850° were frost-proof, whilst facing-bricks of the same material, and burnt at the same heat, were destroyed when they had taken up moisture and were then exposed to frost. Bricks with a porous surface seem to resist better than such as have a very compact and especially a glazed surface. According to Braun, a brick is frost-proof if its cohesive force per square centimetre is greater than the expansive force which the water absorbed by 1 square centimetre exerts in freezing. It would be desirable to saturate a brick thoroughly with water and then to expose it repeatedly to a temperature of – 15°.

The so-called light bricks, which float upon water, were known to antiquity. These bricks are mentioned by Posidonius and Strabo, whilst Vitruvius and the elder Pliny speak of them as very important. The infusorial earth (Kieselguhr) obtained at Oberohe, in Hanover, is at present often used for the production of such bricks. Kieselguhr is also found in Skye and other islands on the west coast of Scotland.

Fire-bricks.—These bricks (known in Germany as Scharmotte-bricks and in France as Chamottes) are used in the erection of fire-places, furnaces, flues, &c., where

* These flooring-tiles, called in Germany "*Fleissen*," must not be confounded with the glazed and coloured tiles used by the ancient Romans, and now revived as a material for hearths and for paving churches, entrance-halls, &c.

common bricks would melt. They are made of a clay rich in silica and alumina, but as far as possible free from lime, alkali, and ferrous oxide. To increase its infusibility and secure it from shrinkage and cracking, it is mixed with clay which has been already burnt, sand, coke, graphite, &c. In the manufacture of fire-bricks it must be considered that there are two agencies which imperil their duration—a high temperature in itself, and then the simultaneous attack of matter which may act as a flux, such as flue-dust, alkaline vapours, melting alkalies, and metallic oxides. In addition, fire-bricks must resist great alternations of temperature and be firm enough to bear a strong pressure.

Particular notice must be taken of the action of slags, &c., upon the resistance of clays to fire. Basic slags attack quartz-stones, whilst acid slags have no such action. Coke burnt in generators yielded 11·9 per cent. of ash of the following composition:

	Ash.		Slag.
	Soluble in Water.	Total.	
SiO_2	—	47·91	62·95
Al_2O_3	—	30·17	25·23
Fe_2O_3	—	12·16	
FeO	—	—	3·12
Mn_3O_4	—	0·38	
MnO	—	—	0·28
CaO	0·24	1·41	0·46
MgO	0·41	1·22	0·92
Na_2O	0·20	2·60	0·82
K_2O	0·26	3·34	3·51
SO_3	0·84	0·82	
P_2O_5	—	—	0·55
Fe	—	—	0·09
FeS	—	—	0·04
	1·95	100·01	99·97

The watery extract is a basic mixture of sulphates; the residual silicate corresponds with the formula $2RSiO_3.5Al_2Si_2O_7.2SiO_2$.

The analysis of the difficultly fusible blackish slag flowing off leads to the formula $2RSiO_3.3Al_2Si_3O_9.2SiO_2$. It contains no globules of metallic iron. Hence in the generator a part of the iron from the ash has been reduced to metal, the calcium and magnesium sulphates have been volatilised or dissipated, and the alkalies have been converted into slags. The Scharmotte bricks, containing 88·9 per cent. of silica, were but slightly attacked by this acid slag.

The worst enemies of basic bricks are the oxides of iron, whence, in using the earthy bases for fire-bricks, the utmost possible freedom from iron should be aimed at; silicic and phosphoric acids and manganese oxides are not so destructive.

From the fire-proof mass there are made not alone bricks, but linings for furnaces in circular segments, plates, saggers for porcelain, stone-ware muffles for burning in the colours for porcelain vessels, and apparatus for chemical works, dye-houses, and paper manufactories (chlorine stills), capsules, dehydrating plates, cocks, gas-retorts, &c. Some analyses of fire-bricks gave the following results:—

	1	2	3	4	5
Silica	63·09	88·1	88·43	69·3	77·6
Alumina	29·09	4·5	6·90	29·5	19·0
Lime	0·42	1·2	3·40		
Magnesia	0·66	—	—	—	2·8
Ferric oxide	2·88	6·1	1·50	2·0	0·3
Potassa	1·92				
Soda	0·31				
Titanic acid	2·21				
	100·58	99·9	100·23	100·8	99·7

No. 1 was clay from Dowlais; 2, bricks from copper furnaces in Wales; 3, in Pembroke; 4, for blast-furnaces; 5, for reverberatories.

The Dinas bricks made from the Dinas rock in the Vale of Neath in Glamorgan, consist of almost pure quartz sand and 1 per cent. of lime. They bear the highest temperatures occurring in metallurgical work without melting or shrinking too much, and are, hence, invaluable for steel furnaces, all kinds of reverberatories, glass ovens, porcelain ovens, &c. Very similar is ganister, a compact, siliceous stone, which, when ground and mixed with clay, serves for lining Bessemer converters, puddling furnaces, &c.

Wasum shows that good bricks may be obtained at a white heat from dolomite and limestone, but not from magnesite. The addition of 5 per cent. of clay yields better bricks without rendering them much less fire-proof. The higher the temperature at which the bricks are burnt the more durable they become. In the construction of furnaces for burning such bricks it is important to arrange the flues so that the temperature may be equal throughout. Dolomite and limestone bricks, if not too much contaminated with matters which increase fusibility, shrink at the strongest white heat only about 2·4 per cent.; bricks made of strongly burnt magnesia shrink only 4 per cent. All substances which decrease the resistance of basic bricks to fire increase their shrinkage. Bricks of limestone and dolomite are equally attacked by the slags formed in iron-smelting, while magnesia bricks are more resistant. The best material for basic bricks is magnesia burnt at the utmost white heat.

Clay pipes may serve either for water-mains or for drain-pipes. Both are made by means of a mould and stamp.

Crucibles.—For crucibles it is necessary that materials shall be used that will withstand the highest temperature. Good crucibles do not crack on being rapidly cooled, and they must also withstand the action of the fluxes that may result from the smelting of metals. The most common crucibles are the Hessian, the graphite or plumbago, and the English. The Hessian crucible is made of 1 part clay (of 71 parts silica, 25 parts alumina, and 4 oxide of iron) and one-half to one-third the weight of quartz sand. They are refractory, remain unaltered by variations in temperature, but are unsuited to some chemical operations on account of coarseness of grain and porosity. If containing too large a proportion of silica, they become perforated by lead oxide, alkalies, &c. Graphite or plumbago crucibles are made from 1 part of refractory clay and 3 to 4 parts graphite. The Patent Plumbago Crucible Company, of Battersea, as well as the Nuremberg manufacturers, employ Ceylon graphite and fire-clay. Graphite crucibles will bear the highest temperature, and they can be made to almost any required size. English crucibles are made from 2 parts of Stourbridge clay and 1 part of coke. Crucibles containing coke exert a reducing action when heated in contact with metallic oxides, and are therefore unfitted to the smelting of metals. Recently lime and chalk crucibles have been employed for this purpose. Caron has used magnesia crucibles in the smelting of iron and steel. Gaudin employs an equal mixture of bauxite or cryolite and magnesia. Very similar are the bauxite crucibles of Audouin.

MORTARS, ETC.

The substances used for the production of mortars are either sufficiently comminuted by the action of water (lime), or they are ground up by mechanical means. They are divided into—

A. *Such as set only in the air.*

1. *Gypsum* must be mechanically pulverised, and sets by combining with water.

2. *Lime* when moistened with water crumbles to a powdery hydroxide, and hardens with sand by the formation of a silicate (ordinary mortar).

B. *Such as set either in the air or under water* (*hydraulic cements*).

3. *Hydraulic Limes*, obtained by burning limestones containing more or less clay and silica, and fall to powder on slacking with water.

4. *Roman Cements*, formed from clayey calcareous marls by burning below the limit of sintering. They do not slack when moistened with water, but have to be pulverised mechanically.

5. *Portland Cements* are obtained from calcareous marls, or from artificial mixtures of lime and clay heated to sintering and then grinding to a fine powder. They contain to 1 part of SiO_2, Al_2O_3, Fe_2O_3, 1·8 to 2·2 of lime, and their specific gravity is above 3.

6. *Hydraulic admixtures* are natural or artificial substances which do not harden alone, but only in conjunction with caustic lime, *e.g.*, puzzuolane, blast-furnace slags, and trass obtained from volcanic tufa.

7. *Puzzuolane Cements* are obtained by a very intimate mixture of pulverulent calcium hydroxide with trass, &c.

8. *Mixed Cements*, made by adding other matters to prepared cements.

Gypsum.—Gypsum is a hydrated calcium sulphate of the formula $CaSO_4 + 2H_2O$. 100 parts contain—

		Lime . . .	32·56
Sulphur . .	18·60	Sulphuric acid .	46·51
Oxygen . .	27·91		
		Water . . .	20·93
			100·00

It belongs to the commonly occurring class of minerals, and is found alone or with anhydrite (karsenite, $CaSO_4$) in strata chiefly of the tertiary formation. The following kinds are distinguished:—(1) Gypsum spar, foliated gypsum, glass stone, isinglass stone, or selenite, possessing a very perfect cleavage, and allowing fine laminæ to be separated; (2) Fibrous gypsum, or satin spar; (3) Froth-stone, a scaly crystalline gypsum; (4) Granular gypsum, or alabaster, of coarse or fine-grained texture; (5) Gypsum stone, plaster stone, or heavy stone, a laminated gypsum; (6) Earthy gypsum, or plaster earth.

Nature of Gypsum.—Gypsum is soluble in 445 parts of water at 14° C., and in 420 parts at 20·5° C.; the solubility is increased by the addition of sal-ammoniac. Its behaviour under the influence of heat is important. Graham states that gypsum placed in a vacuum over sulphuric acid, and heated to 100° C., loses its water, forming the combination $CaSO_4 + H_2O$, with 12·8 per cent. water. According to Zeidler, the statement that this combination does not harden with water is incorrect. By heating to 90° for some time 15 per cent. of the water may be expelled; at 170°, according to the experiments of Zeidler, all the water will be given off. But of more importance are the experiments not carried on *in vacuo*. In the air gypsum begins to lose its water at 100°, and the loss is not complete under 132°. Gypsum from which all the water has been removed is termed burnt gypsum, or spar-lime; it has the property of re-forming with water the same hydrate, thus becoming hardened. Advantage is taken of this property in the application of gypsum as a mortar. According to Zeidler, gypsum as technically employed in stucco-work, &c., is not anhydrous, but contains 5·27 per cent. water. If gypsum is "over burnt," that is, heated above 204°, it loses the property of hardening with water, probably owing to the fact of its being converted into anhydrite, which does not re-combine with water.

The water of crystallisation of the gypsum is saline, and consequently can be removed by the addition of salts; this probably accounts for the hardening of unburnt gypsum when treated with a dilute solution of potassium sulphate or carbonate, &c. The hardening in this follows more quickly than with burnt gypsum and pure water. With potassium sulphate a double salt is formed according to the formula

$K_2SO_4 + CaSO_4 + H_2O$; gypsum and potassium bitartrate give rise to tartar and crystalline gypsum. Potassium chlorate and nitrate, as well as sodium salts, do not effect the hardening of powdered gypsum. Gypsum thus hardened, if re-powdered and again treated with potassium sulphate or carbonate solution, hardens once more. Technical use is made of this property in re-hardening old or in hardening gypsum not sufficiently burnt, by employing instead of water a solution of potassium carbonate.

The Burning of Gypsum.—Gypsum is burnt to effect the removal of the water. Lately many improvements have been made in the methods of burning, it having been found that the good qualities of the gypsum mainly depend upon the preparation. There is, however, a choice in the stone to be burnt, the heavier and denser varieties of gypsum yielding the best commercial article.

Payen, by experimenting with large quantities of gypsum, obtained the following results:—(*a*) The lowest temperature at which gypsum can be burnt with advantage is 80° C., a long time even then being required. (*b*) A temperature of 110° to 120° yields the best technical preparation. (*c*) In order that the burning may take place equally, the gypsum should be first reduced to powder or small pieces. The aim, of course, is in all cases to obtain a small homogeneous product rather than a large quantity unequally burnt. Small quantities of gypsum may be burnt in an iron vessel over a coal fire; the operation should be continued till no aqueous vapour is condensed on a cold glass plate.

Kilns, or Burning Ovens.—In large quantities gypsum is burnt in an oven or kiln, the one necessary precaution being to avoid arranging the layers of gypsum with such fuel as will reduce the gypsum to calcium sulphide ($CaSO_4 + 4C = CaS + 4CO$).

A very simple and very general construction of kiln is shown in Fig. 453. It consists of walls of strong masonry, *A*, spanned by a flat arch, ventilated at *a a a*. In this room is placed the gypsum only, the fire being lighted in a series of small chambers in the lower part of the room: brushwood is the best fuel. *b* is a door, through which the material is introduced. The oven (Fig. 454) used by M. Scanegatty is very similar.

Fig. 453.

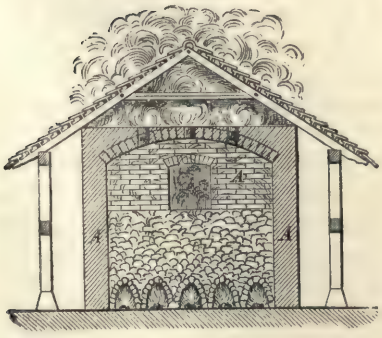
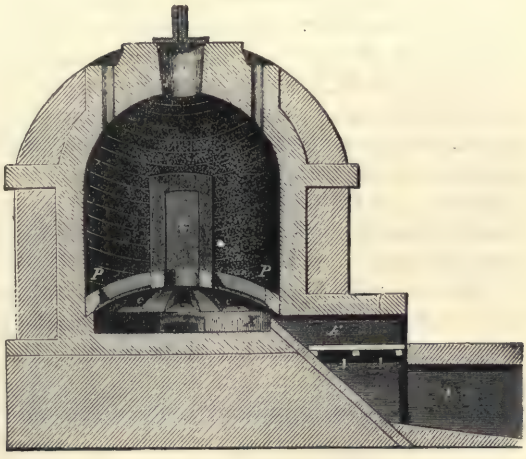


Fig. 454.



The inner room is divided unequally by an arch, *P*, about one foot from the floor; into the upper part the gypsum is introduced through the door, *G*. The under part or fire-room is in connection with a flue, *E*, of a furnace, *A A*, the flames from which, driven by the draught from the gallery, *C*, are carried through *X* to play upon the arch, *P*, the hot air and gases passing through *c c c* into the upper room. The aqueous vapour escapes through *H*.

Lately Dumesnil's oven, shown in plan at Fig. 455, and in section Fig. 456, has been much employed. It somewhat resembles Scanegatty's oven in construction, and consists of an under fire-room and an upper room or oven, in which the gypsum is burnt. The fire-room contains an ash-pit, A, with a door, B, a grate or grid, C, and the hearth, D. A draught, H, assists the combustion. The hot air and gases pass by the flues, E, to the chamber, F. The walls of the oven, J, K, L, are of solid masonry. I is a vault, furnished with a staircase, *g h*, to facilitate access to the furnace. P, the chimney, is of iron plate, with a clack, Q, which can be regulated by the chain U U. O O are ventilating pipes. In the wall of the burning-room are two openings—one, M, through which admittance to the interior is gained to place the lower layers of gypsum; the other, N, for the upper layers of gypsum: both are closed by doors of iron plate. An equal heat is necessary in the burning-room, and is maintained by the peculiar arrangement of the chamber F. This chamber, closed at the top by the cap,

Fig. 455.

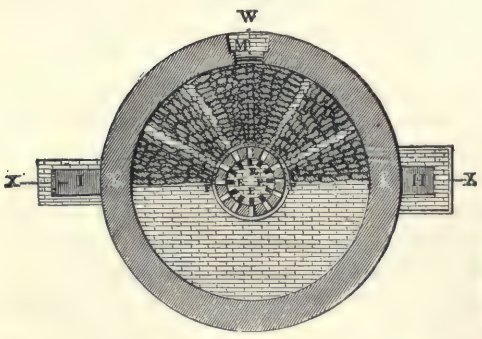
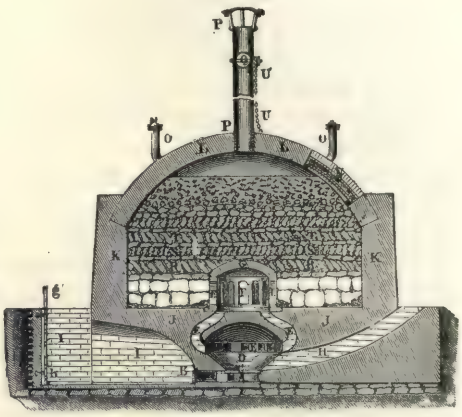


Fig. 456.



G, is provided with twelve openings, each 0·7 metre high, the chamber itself being 1 metre in diameter. The channels thus commenced by the openings in F are continued to the walls of the room by the arrangement of large blocks of gypsum. The layers of gypsum, R, S, T, are placed crosswise alternately with intermediate layers, so as to facilitate the draught in every possible way. The firing is continued gently for four hours, then strengthened for eight hours, when all the openings are closed, and 5 to 6 cubic metres of coarse gypsum powder spread equally over the top of the burning gypsum. By this means the quantity of burnt gypsum is increased without a further expenditure of fuel. After standing twelve hours in the oven to cool the whole contents are removed.

Grinding the Gypsum.—After the burning the gypsum is to a certain extent in powder, but if not sufficiently even it has to be ground. The usual modes of grinding are in a stamp or roller mill. After grinding, the gypsum is sifted, and placed in some position where damp cannot affect it. Sometimes the grinding and sifting are conducted in one apparatus; generally the mill and sieves are separate.

Uses of Gypsum.—Gypsum is employed industrially in very many ways. It is sometimes used unburnt in building; it is then difficult to manipulate with water, but becomes plastic by continued moistening. The heavy and strong fine-grained gypsum, especially the white powdered gypsum, is used in building for decorative purposes. From the alabaster of Voltena, Florence vases of great beauty were fabricated; the same material is used for making Roman pearls. The clear varieties of gypsum are used in the manufacture of cheap jewellery, being ground and polished. The fibrous gypsum is sometimes used for writing sand, as a substitute for pounce, &c. Fine

gypsum powder is an ingredient of porcelain manufacture. Unburnt gypsum finds further application in the conversion of ammonium carbonate into sulphate. Gypsum contains 46·5 per cent. sulphuric acid and 18·6 per cent. sulphur. It is largely employed in agriculture as a manure, both burnt and unburnt. It is generally agreed that the favourable action of the gypsum upon vegetation is due to the absorbed ammonia which is again yielded up.

Putridity gives rise to the formation of carbonic acid, which combines with the lime of the gypsum, leaving calcium carbonate and ammonium sulphate. This explanation of the efficacy of gypsum-manuring, as it is termed, is, however, insufficient. The investigations of Mayer have shown that in clayey soils the iron oxide, &c., affords larger and better combinations with ammonia than gypsum. The quantity of gypsum used is generally about 5 cwts. to the acre, containing and realising at the most 2·7 cwts. of ammonium carbonate. Mayer's researches, however, show that in an acre of

Field land . . .	227 cwts.
Chalky soil . . .	158 „

of ammonia were contained. According to Liebig's late researches (1863) it appears that the gypsum gives up to the earth a portion of its lime in exchange for magnesia and potash. But it must be borne in mind that pulverised gypsum, as well as unburnt gypsum, when brought into contact with a solution of potash, sets into a difficultly soluble mass. We must, then, wait for an adequate theory until the several reactions have been more closely studied.*

Gypsum Casts.—The employment of gypsum in casting, and in all cases where impressions are required, is very extensive. A thin paste of 1 part gypsum and $2\frac{1}{2}$ parts water is made: this paste hardens by standing, forming $CaSO_4 + 2H_2O$. The hardening of good, well-burnt gypsum is effected in one or two minutes, and more quickly in a moderate heat. Models are made in this substance for galvano-plastic purposes, for metallic castings, and for ground works in porcelain manufacture. The object from which the cast is to be taken is first well oiled, to prevent the adhesion of the gypsum. Where greater hardness is required a small quantity of lime is added; this addition gives a very marble-like appearance, and the mixture is much employed in architecture, being then known as gypsum-marble or stucco. The gypsum is generally mixed with lime-water, to which sometimes a solution of zinc sulphate is added. After drying, the surface is rubbed down with pumice-stone, coloured to represent marble and polished with Tripoli and olive-oil. Artificial scaliogla work is largely composed of gypsum. Gypsum is also much employed in the manufacture of paper.

Hardening of Gypsum.—There are several methods of hardening gypsum. One of the oldest consists in mixing the burnt gypsum with lime-water or a solution of gum-arabic. Another, yielding very good results, is to mix the gypsum with a solution of 20 ounces of alum in 6 pounds of water; this plaster hardens completely in fifteen to thirty minutes, and is largely used under the name of marble cement. Parian cement is gypsum hardened by means of borax, 1 part of borax being dissolved in 9 parts of water, and the gypsum treated with the solution. Still better results are obtained by the addition to this solution of 1 part of cream of tartar.

The hardening of gypsum with a water-glass solution is found difficult, and no better results are obtained than with ordinary gypsum. Fissot obtains artificial stone from gypsum by burning and immersion in water, first for half a minute, after which

* The use of gypsum in manures has proved less satisfactory in Britain than on the Continent. It plays no small part in the sophistication of articles of consumption, such as flour, wines, sweetmeats, &c. Its chief locality in Britain is in the neighbourhood of Newark-upon-Trent.

it is exposed to the air, and again for two to three minutes, when the block appears as a hardened stone. It would seem from this method that the augmentation in hardness is due to a new crystallisation. Hardened gypsum, treated with stearic acid or with paraffine, and polished, much resembles meerschaum: the resemblance may be increased by a colouring solution of gamboge and dragon's blood, to impart a faint red-yellow tint. The cheap artificial meerschaum pipes are manufactured by this method.

Scott's "gypsum cement" or "selinitic mortar" was made by the action of the fumes of burning sulphur upon ignited lime. Schott has since pointed out that it can be more simply obtained by igniting quicklime with burnt calcium sulphate.

Tripolite is merely gypsum with impurities of sand, calcium, and magnesium carbonate, and burnt with 0·1 of its weight of coal or coke.

Lime.—Lime, calcium oxide ($CaO = 56$), in its combination with carbonic acid as calcium carbonate ($CaCO_3$), is a substance of very frequent occurrence. It is a constituent of bone, of the shells of the mollusca, and is found most extensively in the mineral kingdom as marble, limestone, coral, Iceland spar, arragonite, chalk, &c. Its technical applications are as marble in building, in the manufacture of artificial mineral waters, as Iceland spar for optical purposes, as chalk in colours and drawing materials, in the manufacture of soda, in the preparation of hydraulic mortars, building and plastering materials, &c. Limestone, Alpen lime, lias lime, Jura lime, &c., is, when mixed with clay, iron, and other metallic oxides, used as a colour. Lithographic stone is a yellow-white limestone, employed, as its name implies, in lithography. Chalk or earthy calcium carbonate occurs in strata in North Germany, Denmark, France, and England. To this class belongs marl-limestone, distinguished by containing clay. With sodium carbonate, calcium carbonate forms Gay-Lussite ($CaCO_3 + Na_2CO_3$); with barium carbonate, baryto-calcite ($BaCO_3 + BaCO_3$); and with magnesium carbonate, bitter-spar or dolomite ($CaCO_3 + 3MgCO_3$), the latter occurring with 3 mols. of magnesium carbonate to 1 mol. of lime.

Properties.—Calcium carbonate is not soluble in pure water; but if the water should hold carbonic acid in solution, bicarbonate is formed. When this solution, by means of evaporation, loses half its carbonic acid, an insoluble carbonate is formed. In this manner are naturally formed *stalactites* and *stalagmites*. The deposit of calc-sinter upon objects deposited in caverns, in limestone-rock, &c., is thus explained. When calcium carbonate is ignited to whiteness in a porcelain crucible, the carbonic acid is disengaged, and there remains calcium oxide (CaO) or caustic lime. 100 parts of calcium carbonate yield 56 parts of burnt lime. The volume of the lime undergoes no diminution by burning. Burnt lime is the form under which lime most commonly appears in the market. Calcium carbonate, heated in a closed porcelain tube, melts, and forms a crystalline mass, a carbonate, afterwards unalterable.

Lime-Burning.—The burning of lime is effected—

In kilns,
In field-ovens, and
In lime-ovens.

Lime-burning in kilns is accomplished in the following manner:—The limestone, unless it has previously been broken into small pieces, is heaped up into cairns similar to the heaps of wood to be converted into charcoal. The kiln is then covered with earth or turf, and the fire so placed that the larger pieces of lime in the interior of the heap are burnt. The regulating of the draught, the kindling, the covering, and the cooling are on the same principle as that followed by the charcoal-burner in the conversion of wood into charcoal by combustion. According to P. Löss, a kiln of this kind, 4·5 metres in height, contains 35·5 cubic metres of lime as well as 2·6 cubic metres of lime-dust. In the field-ovens the burning is similarly conducted, but sometimes on a larger scale,

the kilns being always temporary. It is easy to see that the burning in this manner is only of slight technical importance; besides the great waste, only a small quantity could be produced at an operation. Therefore, permanent ovens are employed. These are divided into—

a. Those kilns in which the burning is interrupted, or occasionally employed (the occasional kiln).

b. Those kilns in which the burning is continuous (the continuous kiln).

In the occasional kiln, after the burning is finished, the kiln is cooled, and the lime then removed. In the continuous kiln, on the contrary, the calcination is continuous, the kiln never being allowed to cool. It is so constructed that the burnt lime can be removed and fresh limestone introduced, without in the least interrupting the process. The continuous kiln has many recommendations—among them that of effecting a saving in fuel. In a small way, where, as a rule, burning cannot be constantly carried on, the small occasional kiln is of course to be preferred.

Occasional or Periodic Kilns.—The occasional or periodic kiln with interrupted burnings sometimes have, and sometimes have not, a grated furnace. Figs. 457 and 458

Fig. 457.

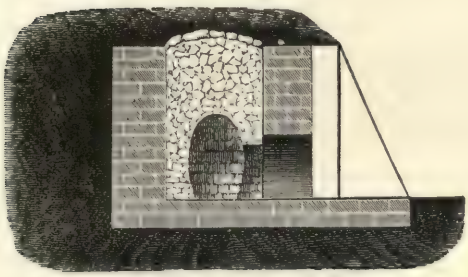
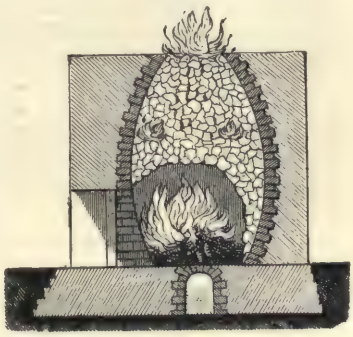


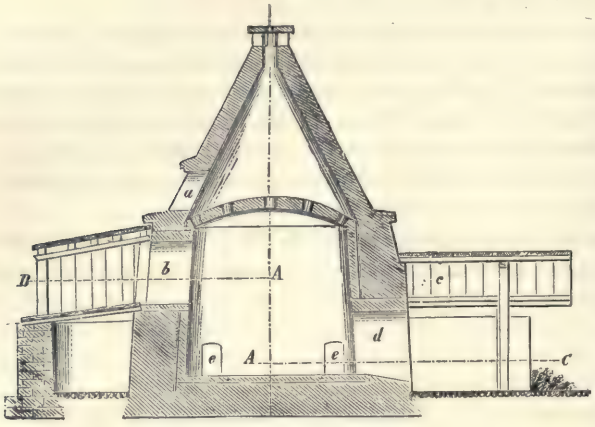
Fig. 458.



show two lime-kilns of the ordinary construction without grated furnaces. They are built either on the slope of a hill or on the slope of the limestone quarry itself. As a rule, the kilns are built near one another, so that one wall serves for two kilns. The height of the vault varies from 1·3 to 1·6 metre, and it is generally built of the largest limestones, while the smaller stones and lime-dust are placed in the interior of the kiln. Through the furnace doors, easily combustible fuel, such as brushwood, light timber, shavings, &c., is introduced. The mass becomes gradually heated, the larger stones crack and break up, and the whole mass sinks together. As the firing is increased the lime becomes of a brighter colour and the flames free from smoke. As soon as the lime immediately under the stones on the top of the kiln is at a white heat the burning is complete. The mass by this time will have sunk one-sixth. A burning generally occupies thirty-six to forty-eight hours. An occasional kiln with a grated furnace effects a quicker and more complete combustion of the fuel; but they are open to the objection that the consumption is greater. On the other hand, the kilns without a grated furnace are less perfectly heated. A kiln much used in Hanover is shown in Fig. 459, and in plan in Fig. 460; Fig. 461 shows the under part of the kiln in vertical section. The lower room serves for the calcination of the lime; over this is a vaulted chamber 3·12 metre in diameter and 11 feet in height. *e e e e*, Figs. 460 and 461, are four stoke-holes for the introduction of fuel, stone-coal, brown-coal, breeze, &c. *B* is the approach by which the limestone is introduced into the furnace; *d* the door by which entrance is obtained to remove the burnt lime. Both these openings are closed during

the actual burning. *a* is an approach to the "upper jacket," as the upper chamber is termed. This opening is necessary as a draught to assist the flame and hot gases in their escape from the top of the kiln; it also causes a more intense flame in other parts of the kiln. Figs. 460 and 461 show how the limestone is kept clear of the hearths.

Fig. 459.



A piece of wood is placed vertically in the centre of the oven to direct the flames upwards when the fire is lighted. During the first six hours the fire is weak; then a stronger fire is obtained until the yellow lime-flames spring from the openings in the vault, and the oven is in a clear glow.

The Continuous Kilns.—The construction of the kilns for continuous burning is somewhat different to that of the preceding. They are of two kinds. In one the fuel and the limestone are placed in alternate layers; in the other kind, the fuel and the limestone are not in contact, there being furnaces for the former and separate chambers for the latter. In either, fresh limestone is added in proportion as the burnt stone is removed from the bottom of the kiln.

Fig. 460.

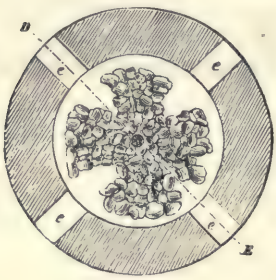


Fig. 461.

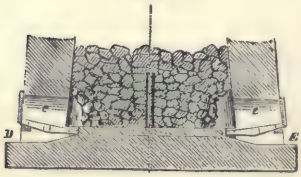
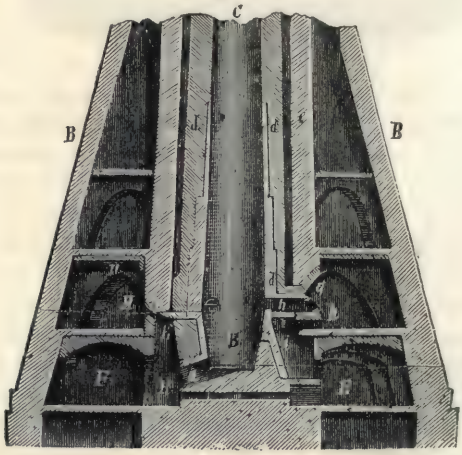


Fig. 462.



At Rüdersdorf, near Berlin, a very efficient kiln is employed, shown in section in Fig. 462. The lining wall of the shaft, *d*, is built of fire-brick; the counter wall, *e*, is separated from the lining wall by a chamber filled with ashes, building refuse, &c. The outer wall, *B B*, is not an essential portion of the kiln; it serves merely as a jacket for the retention of the heat, while the galleries, *H* and *F*, can be used as drying-rooms for wood, fuel, &c. During the process, the under part, *B*, of the shaft is filled with prepared lime, which is removed by the draught-hole, *a*, in the sole of the shaft. For the purpose of hastening the descent of the burnt lime, the sides of the lower part

of the shaft are sloped towards the draught-holes. The shaft is usually 14·123 metres in height. About 4 metres above the sole of the shaft is situated the fire-room, *h*. Three to five fire-rooms are in action in a single shaft. The fuel is wood or turf. *i* is the ash-pit, whence the ashes fall into *E*. The flame enters the shaft through the opening, *b*, at the end of the fire-room. The freshly burnt lime is received in *F*. *K K* is a draught gallery communicating with *H*. The kilns are locally known as three-, four-, or five-fired kilns, according to the number of fire-rooms. Should the kiln not have been in use for some time, the firing is commenced by adding fuel, such as wood, turf, &c., to the limestone in the shaft. When the shaft is thoroughly warmed and a good draught obtained, lime only is introduced into the shaft. The shaft is entirely filled with limestone, and sometimes the limestone accumulates upon the mouth or top of the kiln to a height of 1·3 metre.

Kilns for Burning Lime and Bricks.—When the locality is favourable, the kilns are arranged to burn both lime and bricks at the same time. The annular kiln of Hoffmann and Licht, described under Brick-making, is the most suitable for this double purpose.

Properties of Lime.—The quality of the burnt lime is greatly influenced by the constitution of the limestone burnt. When the limestone consists chiefly of pure carbonate of lime, the resulting lime is what is termed a "fat" lime. On the other hand, if the limestone is of similar composition to dolomite ($CaCO_3 + MgCO_3$), containing magnesia, the resulting lime forms a short, thin "milk" with water, and is termed "poor." With 10 per cent. of magnesia the lime is noticeably poor, and with 25 to 30 per cent. almost useless. The lime on being taken from the kiln is by no means found to be burnt equally. Some pieces that have almost escaped the fire are merely superficially burnt, and contain a kernel of unburnt limestone. Other pieces exposed to the full heat of the kiln are "over-burnt." The "over-burning" of the lime is either due to the forming of "half-burnt" lime ($CaCO_3 + CaH_2O_2$) by a strong and sudden ignition; or by means of the high temperature the small quantity of silica and alumina contained in the limestone become sintered over the surface, and the lime is thus prevented by a coating of silicate from combining with the water to form a cream.

Slacking Lime.—Burnt lime moistened with water slacks with great violence, 100 parts by weight of lime requiring only 32 parts water, or 3 vols. of lime to 1 vol. water, to obtain by the combination a temperature of 150°. The result of the slacking is a soft, white powder, lime-meal or powdered lime, hydrated calcium oxide (CaH_2O_2), which in volume exceeds three times that of the lime slaked. If less water is added than is requisite for the formation of the hydrate, a sandy powder is obtained of little value technically. It is therefore very disadvantageous to place lime in baskets in damp situations. For technical application to building purposes, after the lime has been slaked with one-third of its weight of water, an equal quantity of water is added to the mass to form a thin cream. Slaked lime retains its water of formation with such obstinacy that at a temperature of 250° to 300° no loss of weight occurs. The hydrate forms a thin cream with water, and from this cream by further dilution lime-water or milk of lime is obtained. If the lime-water be filtered, there results a saturated solution of hydrate of lime, containing 1 part hydrate to 778 parts water.

The temperature required for burning lime has been determined by Le Chatelier. The tension of dissociation of calcium carbonate is—

Temperature.		Pressure, millimetres.
547°	...	27
625	...	56
740	...	255
810	...	678
812	...	763
865	...	1333

Although the dissociation temperature at 812° is equal to the pressure of the atmosphere, a heat of 925° is needed for the complete expulsion of the carbon dioxide.

Mortar.—Mortar is a mixture of sand with cream of lime, used in building as a binding material. The ordinary mortar sets or hardens only in the air; hydraulic mortar sets under water.

A. *Common Mortar.*—When slaked lime is exposed to the atmosphere it absorbs carbonic acid, and the mass becomes much shrunken and cracked. The carbonate thus formed, on becoming perfectly dry, attains the hardness of marble. Such a material, with certain modifications, is consequently admirably adapted as a cement to bind together bricks, blocks of stone, &c., in building. But as the contraction or shrinkage would give rise to great unevenness in the construction of walls, it becomes necessary to add sand or some similar substance to the lime-cream. This addition gives a body to the mortar, which combines with the bricks into one coherent mass. Common mortar is ordinarily made with slaked lime, an intimate mixture with sand and water being formed. Angular or sharp sand is preferred to smooth, round sand, as making a more tenacious mortar. Round-grained sand yields a very brittle mortar. The proportion of sand to the lime is a matter immediately affecting the quality and hardness of the mortar. In practice, 1 cubic metre of stiff lime-cream requires 3 to 4 cubic metres of sand; but poor lime containing magnesia will only admit of 1 to $2\frac{1}{2}$ cubic metres of sand. When mortar is employed in brick-laying, the surface of the brick is moistened, the mortar laid between each brick, and left to dry. When dry it is often harder than the brick itself.*

Hardening of Mortar.—Mortar sets or hardens very quickly. After a day it will attain a firmness that will last for centuries. The drying out of the water from the mortar is not the sole cause of its hardening, as may be very easily ascertained by drying the mortar in a water-bath or over the spirit-lamp; the result is not a stone-like, but a friable, non-coherent mess. Fuchs accounts for the hardening of mortar by supposing the formation of a basic calcium carbonate ($CaCO_3 + CaH_2O_2$), a combination which has not been known to suffer conversion into ordinary carbonate of lime ($CaCO_3$). Recent researches have shown this supposition to be erroneous, as it does not agree with the results of analyses, which have yielded a quantity of carbonic acid incompatible with the existence of a neutral carbonate; 20 and even 70 per cent. of carbonic acid have been found. The experiments of Alexander Petzholdt, A. von Schrötter, and others have proved that there is an increase of soluble silica. The conversion of quartz-sand into soluble silica under the influence of hydrate of lime is not, however, a reaction at all explanatory of the hardening of mortar, as washed chalk instead of silica forms an equally hard mass. W. Wolters gives the formation of silicate of lime as accounting for the hardening of mortar. It is not seldom in the analysis of old mortar from the interior of walls that caustic alkalies are found.

B. *Hydraulic Mortar.*—Limestone containing more than 10 per cent. silica possesses, when burnt and made into a mortar, the peculiar property of hardening under water. Lime burnt from such limestone is termed *hydraulic* lime, and the mortar *hydraulic* mortar.

When unburnt, hydraulic lime is a mixture of calcium carbonate with silica or a silicate, generally aluminium silicate, the latter being insoluble in hydrochloric acid. During the burning, the hydraulic lime suffers a change similar to that taking place when a silicate insoluble in acid is precipitated, during the application of heat, with an

* The durability of the old Roman masonry was in a great degree owing to the fact that they slacked their lime in small quantities as it was needed, mixed it with clean, sharp sand, and used it whilst still warm. The wretched character of the work done by modern building speculators is owing, on the contrary, to the fact that they slack a large quantity at once of the worst lime procurable, and let it lie sometimes for weeks before use. Instead of sand they sometimes take sifted garden and field soil, containing abundance of decaying organic matter.

alkaline carbonate. After burning, the lime is to a great extent soluble in hydrochloric acid, and has lost some of its carbonic acid. Von Fuchs, Feichtinger, Harms, Heldt, W. Michaëlis, and A. von Kripp's experiments have proved that the silica of hydraulic lime is precipitated in a gelatinous condition, and that constituents such as alumina and iron oxide are of influence only when, under ignition, they have formed a chemical combination with the silica.

Hydraulic mortars are made—

1. With a thin cream of lime and water to which sand is added; or with

2. A mixture of ordinary air-mortar with water and cement.

During the slacking of the hydraulic lime water is absorbed, but without any considerable evolution of heat or increase in volume. Hydraulic mortar is employed in the same manner as ordinary mortar—the lime-cream must be freshly made, and the brick or masonry work moistened. The mortar should be placed thickly between each layer of bricks, in order to afford a good firm bed and allow for shrinkage.

Hydraulic limes form a transition from ordinary lime to Roman cement.

Roman cement is obtained by burning calcareous clays above a sintering-heat and grinding the product. The powder, which is usually of a reddish brown, yields a hydraulic mortar which sets more rapidly than Portland cement, but does not attain the same firmness if magnesia is present.

Michaëlis found by the analysis of various Roman cements—

	1.	2.	3.	4.
Lime	58·38	55·50	47·83	58·88
Magnesia	5·00	1·73	24·26	2·25
Silicic acid	28·83	25·00	5·80	23·66
Alumina	6·40	6·96	1·50	7·24
Iron oxide	4·80	9·63	20·80	7·97

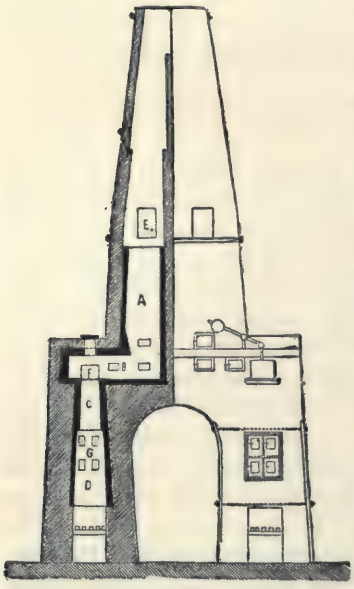
The analyses are from cements free from water and carbonic acid. No. 1 is Roman cement from Rüdersdorf limestone; 2. From limestone from the Isle of Sheppy, yellow-brown in colour, coarse, and hard; 3. From limestone forming the under bed of the lead ores at Tarnowitz, of a blue-grey colour, firm, and of a crystalline appearance; 4. From Hausbergen limestone.

Portland cement, the best of all the mortars, is distinguished by the high temperature, reaching white heat, used in its preparation.

Portland cement, so named from the resemblance it bears when set to Portland stone, is a scaly crystalline powder of grey colour, and was first prepared by Mr. Joseph Aspdin, of Leeds, in 1824. According to his letters patent, he prepared his cement in the following manner:—A large quantity of limestone was taken and pulverised; or the dust or pulverised limestone used to mend the roads was employed. This material was dried and burnt in a lime-kiln. An equal quantity by weight of clay was added to the burnt lime, and thoroughly kneaded with water to a plastic mass. This was afterwards dried, broken in pieces, and burnt in a lime-kiln to remove all the carbonic acid. The mass, thus transformed to a fine powder, is ready for the market. It is known in commerce as a grey, or green-grey, sandy powder. But Pasley must be considered the true founder of artificial cement manufacture in England. He, in 1826, obtained a cement by the burning of river mud from the Medway, impregnated with the salts from sea-water, with limestone or chalk. The mud from the Medway is probably the best adapted for the manufacture of Portland cement, on account of the sodium salts it contains; and from this supposition there seems good ground for Pettenkofer's recommendation that various marls, burnt after lixiviation with a solution of common salt, should be tried. At the present time the mud from the mouths and delta formations of several large rivers is employed in the preparation of this cement.

The manufacture of Portland cements usually follows this mode. The raw materials, limestone and clay or mud in equal quantities, are intimately mixed, the mixture dried in the air, and then burnt in a shaft-oven. The shaft-oven is generally 14 to 30 metres in height, with a width of 2·3 to 4 metres. At a height of 1 to 1·3 metre from the ground is a strong grating, through which the lumps of limestone mostly fall, those remaining being afterwards broken by the heat. The oven is so arranged that a layer of fuel and a layer of cement stone alternate. Coke is generally chosen as fuel, being found by experience best adapted for the purpose. After the mass has been submitted to a red heat for one hour, it assumes a yellow-brown colour, and at a higher temperature becomes a dark brown. Gradually the lime becomes causticised, and enters more and more into chemical combination with the silicates. At a white heat the mass becomes grey in colour, with a streak here and there of green. If during the operation these colours are shown at the several stages, the resulting cement will be good and set hard. If the heating is continued, the cement will assume a blue-grey colour, and become quite useless. If removed at the first stage the mass yields a yellow-brown light powder; at the second, a grey sharp powder, tinged with green. Beyond this stage the powder is blue-grey, or grey-white, clear and sharp, and very similar to glass-powder. The more lime the mixture contains, or, it might be said, the more basic the mixture, the more durable is the cement, and the less it falls to pieces in burning. A mixture in which clay predominates is always more or less a weaker cement, falling to pieces readily, or, technically, not binding well. According to Michaëlis, the addition of lime or alkalies prevents the cement separating, and renders it more binding; but in practice this addition would not be sufficiently economical. The more intimately the clay and lime are mixed, the larger the amount of lime that may be incorporated. From the moment of stiffening till the final hardening, the cement, if set in the air, experiences no change; but if in water, there is at first a small loss of the more soluble constituents—the alkalies.

Fig. 463.



Portland cement mixed with water to a paste stiffens in a few minutes, and after the lapse of a day sets tolerably hard. After a month the cement sets into a substance so hard and firm that it emits a sound when struck by a hard body. It is admirably adapted, when mixed with sand or gypsum, for being cast into various architectural ornaments, and, indeed, has from this property been termed artificial stone. Lately Grüneberg has made crystallising vessels of this cement, and Posch employs it in constructing reservoirs for hot fluids.

Portland cement is considered by military engineers the best material to oppose to the projectiles used in modern warfare.

It has been very successfully burnt in the stage-furnace of Dietzsch (Fig. 463). The raw materials, artificially dried, are introduced through a hopper, *E*, into the preliminary warming-chamber, *A*. It slips down over the arched connecting-shoot, *B*, and is shovelled from the working-door, *F*, into the melting-space, *C*. Any clinkers which have become welded to the sides of the furnace are removed through the opening, *G*, so that they fall into the cooling-room, *D*. 100 parts of cement require in this furnace only 9 to 19 parts of coal, as against 6–23 parts in a ring-furnace, and 20 to 28 parts in a shaft-furnace.

These varying statements may be in part explained by the difference in the fuel and by the more or less careful superintendence of the work. If, *e.g.*, Meyer found in the combustion-gases of a ring-furnace only 3·2 to 7·6 per cent. carbon dioxide, as against 2 to 11·9 per cent. in the gases of the stage-furnace (where we have also to take into account that a considerable part is derived from the decomposition of the lime in the raw material), this proves that there is a great waste of fuel. If only half as much carbonic acid were introduced, we should have a much greater heat, more rapid burning, and less loss of heat at the chimney. These differences seem in part to be explained by the different nature of the mass itself. At least Dietzsch observed that in his furnace two masses used 15·9 to 19 kilos. of coal and a third only 9. As the chemical processes in burning (decomposition of $CaCO_3$ into $CaO + CO_2$, formation of silicates and aluminates) do not explain so great a difference, the reason probably is that one mass requires a higher temperature than the other, and that for its production—especially if the supply of air is unsuitable—a disproportionate quantity of coal is needed.

M. W. Michaëlis gives the following analyses of Portland cements, the samples being free from water and carbonic acid :—

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Lime	59·06	62·81	61·91	60·33	61·64	61·74	55·06	57·83	55·28
Silicic acid	24·07	23·22	24·19	25·98	23·00	25·63	22·92	23·81	22·86
Alumina	6·92	5·27	7·66	7·04	6·17	6·17	8·00	9·38	9·03
Iron oxide	3·41	2·00	2·54	2·46	2·13	0·45	5·46	5·22	6·14
Magnesia	0·82	1·14	1·15	0·23	—	2·24	0·77	1·35	1·64
Potash	0·73	1·27	0·77	0·94	—	0·60	1·13	0·59	0·77
Soda	0·87		0·46	0·30	—	0·40	1·70	0·71	—
Calcium sulphate	2·85	1·30	—	1·52	1·53	1·64	1·75	1·11	3·20
Clay / Sand	1·47	2·54	1·32	1·04	1·28	1·13	2·27	—	1·08

No. 1 is Portland cement from White & Brothers, analysed by Michaëlis. No. 2 is Stettin cement, analysed by Michaëlis. Nos. 3 and 4 are Wildauer cements. No. 5, known as Star cement, and No. 6, another Stettin cement, by the same analyst. No. 7, English cement, and No. 8, cement from works near Bonn, were both analysed by Hopfgartner. No. 9 is a strong and porous cement, analysed by Feichtinger.

Boehme gives the analysis of ten samples, which are of little value, as they do not give the locality or the name of the maker.

Hardening of Hydraulic Mortars.—The hardening of hydraulic mortars has often been the subject of investigation. Two views may be taken: first, the mere setting, the congealing of the mass from a fluid state to a moderate degree of hardness; and then the hardening to a stony state. The knowledge we possess of the setting of these mortars is chiefly due to the experiments of Von Fuchs, Von Pettenkofer, Winkler, Feichtinger, Heldt, Lieven, Schulat-Schenko, Ad. Remete, Heereen, W. Michaëlis, and Von Schoenaich-Carolath. The cements when thus considered are best divided in two classes :—The first class, of which Roman cement is the type, embraces the mixture of caustic lime with puzzuolane, pulverised tile, and brick, and such hydraulic mortar as is obtained by burning hydraulic lime and marl. All the cements contain caustic lime unacted upon. The second class comprehends Portland cements, containing no fresh caustic lime. M. Von Fuchs has explained the chemical actions taking place during the hardening of Roman cements as being principally the combination of the lime with silicic acid, the combination giving rise to the peculiar property of hydraulic mortars. He draws this conclusion partly from the fact that from all hydraulic mortars the silica can be thrown down as an insoluble gelatinous mass by the action of carbonic acid.

A similar gelatinous mass results from the combination of silicic acid and lime.

Silicates do not yield gelatinous silica when treated with hydrochloric acid alone, but attain this property when subjected for a length of time to the influence of lime under water; the water also dissolves out the alkalies. Kuhlmann, who has long been employed in the study of the chemistry of hydraulic cements and artificial stones, states that lime can be rendered hydraulic by the intimate mixture of 10 to 12 per cent. of an alkaline silicate, or by treatment with a water-glass solution. Collecting the results of these experiments, the setting of Roman cements appears due to the combination of acid silicates or silica with burnt lime, forming a hydrated calcium silicate intermixed with the alumina and iron oxide.

The hardening of Portland cements has been investigated by Winkler and Feichtinger. According to the former, the chemical action, which is effected under the co-operation of the water, consists in the separation of the silicates into free lime and combinations between the silica and the calcium, the alumina and the calcium. The separated lime combines with the carbonic acid in the air to form calcium carbonate. The hardened Portland cement contains the same combinations as hardened Roman cement; these combinations are formed, however, under the influence of water on opposed conditions. From the results of Winkler's experiments, it would appear that the silicic acid in the Portland cements can be replaced by alumina and iron oxide. Alumina does not affect the hardness, but may lessen the capability of the cement to withstand the action of carbonic acid. During the hardening the influence of the water separates the lime, till finally the combinations $Ca_3Si_3O_9$ and $CaAl_2O_4$ remain, the latter being gradually decomposed by carbonic acid, remaining, however, as long as there is any hydrate of lime in the cement. G. Feichtinger maintains a theory differing from that of Winkler. His experiments lead him to the opinion that in all hydraulic mortars the hardening depends upon the chemical combination between lime and the silica, and between lime and the silicates contained in the cement. In all hydraulic cements free lime is contained; and upon this fact we may base the following experiments. When Portland cement is brought to a paste with a concentrated solution of ammonium carbonate, and stirred for a long time, no hardening is traced, the greater part of the lime forming calcium carbonate. Then let the excess of ammonium carbonate be washed away, the cement dried, and made into a mortar with pure water. This mortar will not harden unless some calcium hydroxide be added, when it hardens similarly to fresh mortar. The same result may be obtained by substituting a stream of carbonic acid gas for the ammonium carbonate; by this means 27 per cent. of calcium carbonate may be obtained. Consequently the views of Winkler must be regarded as the most correct. These experiments also show that in Portland cements silicates or free silica are contained; that, further, free lime does and must exist. Portland cement will not take a glaze, and can only be so far affected by burning as to cause the sintering of the clay contained in the cement.

Erdmenger ascribes the setting of cement chiefly to the formation of a crystalline lime hydrate. This hypothesis agrees ill with the experiments of Ostwald, who found the composition of three cements from Riga (I. to III.) and two from Stettin (IV. and V.) to be as follows:—

	I.	II.	III.	IV.	V.
CaO	72·10	65·42	61·92	65·05	60·52
MgO	3·27	3·89	4·03	3·04	3·02
Al_2O_3	6·66	7·52	7·97	8·09	7·57
Fe_2O_3	1·99	2·15	2·71	3·25	4·48
SiO_2	10·38	14·76	16·75	17·04	20·72
Alkalies	0·85	0·86	1·25	0·92	1·02
SO_3	0·42	0·52	0·42	0·30	0·37
CO_2	1·64	2·19	2·42	0·83	0·52
C	0·36	0·50	0·47	0·67	0·53
H_2O	2·56	2·32	2·24	1·06	1·22

In connection with these analyses, Ostwald determined the heat of setting:

Time.	I.	II.	III.	IV.	V.
2 hours	20·53°	20·47°	9·94°	34·01°	7·53°
6 „	37·05	29·57	12·23	35·46	10·09
1 day	41·35	39·78	15·32	38·39	18·79
4 days	46·16	—	29·72	—	—
5 „	47·17	—	32·10	—	—
6 „	57·96	44·34	33·56	—	—
7 „	65·63	51·55	40·26	—	—

Thus the development of heat was at first very rapid; after six hours more than half the total heat has been liberated. Afterwards the liberation of heat becomes slower and slower, and after thirty days it is as good as imperceptible. We must note the striking increase of the liberation of heat on the fifth, sixth, and seventh day. At this time there evidently begins a new epoch in the chemical process of hardening, which involves a renewed development of heat. The more quickly a cement sets, the greater is its "setting-heat." According to Berthelot 1 gramme lime in slacking evolves 268 heat-units. If we calculate from the analyses how much free lime is contained in the cements, the existing carbonic acid being assumed as combining first with the alkalies and then with the lime, and the water being supposed to combine with the lime to a hydrate, we may determine what quantity of heat would be developed by the action of the water if the lime were free and became hydrated. The calculation is carried out in the following table:—

	I.	II.	III.	IV.	V.
Hydration heat of lime	168·8	150·0	136·6	162·4	155·4
Setting heat of cement	70·2	66·2	45·4	52·8	42·3

The specimens IV. and V. have not been examined to the end, but they have plainly already given off the chief portion of their combining heat, which is in all cases much smaller than the hydration heat of the lime regarded as uncombined. Hence, the assumption that no chemical interaction takes place between the lime and the clay during the formation of Portland cement is not tenable. On the contrary, there occurs a very important reaction, during which a quantity of heat is set free. The so-called physical theory of the formation of cement must be considered as refuted, and the chemical theory alone must be accepted as in harmony with facts. The objection might of course be raised that chemical processes take place during the setting, to which the difference observed might be ascribed. But such processes, like the formation of zeolitic silicates, aluminium hydrates, &c., all evolve heat and therefore tend to lessen the difference. That such difference is still so great proves the importance of the chemical processes during burning.

Le Chatelier ascribes the most important part in the setting of hydraulic mortars to the crystallisation of dissolved matters of the combination $CaO.SiO_2.3H_2O$ (the composition of which is deduced, not from analyses, but from the crystalline compound, $BaO.SiO_2.6H_2O$), which is resolved by water into free lime and an acid silicate, $2SiO_2.CaO$, and by carbon dioxide and water into silica and a calcium carbonate. But the former decomposition ceases when the water contains 0·052 gramme lime per litre. The formation of this silicate during the setting ensues either by the union of the two constituents or by the decomposition of silicates richer in lime, or perhaps by the mere hydration of the anhydrous compound. The above-named combinations of lime with ferric oxide or alumina, which can exist in water in presence of an excess of lime, are decomposed by an excess of water; but the decomposition ceases with a proportion of lime of 0·225 gramme or of 0·6 gramme per litre at 15°. Ferric oxide and alumina are essential in burning, for the better combination of the lime with the silica.

Further experiments are necessary for the full elucidation of the question.

Testing Cement.—In examining cements it is necessary to have in view the mixture

of cement with ground slags, now unfortunately in extensive practice. According to Fresenius, a genuine cement should show (*a*) a specific gravity of at least 3·125, certainly not less than 3·1 ; (*b*) a loss on ignition of between 0·34 and 2·59 per cent., certainly not higher ; (*c*) an alkalinity in the watery solution of 0·5 gramme, corresponding to 4—6·35 c.c. of decinormal acid ; (*d*) a consumption of normal acid on the direct treatment of 1 gramme ground cement between 18·80 and 21·67 c.c., certainly not much lower ; (*e*) a consumption of permanganate solution by 1 gramme cement equal to between 0·79 and 2·80 milligrammes potassium permanganate, not more.

Hydraulic Admixtures.—Trass or tarass is a kind of trachytic tufa found in considerable quantities in the Brohl- and Nettethall, near Andernach.* It contains magnetic iron in small quantities, and also titanic iron.

	Soluble in Hydrochloric Acid.		Insoluble in Hydrochloric Acid.
Silica	11·50	...	37·44
Lime	3·16	...	2·25
Magnesia	2·15	...	0·27
Potash	0·29	...	0·08
Soda	2·44	...	1·12
Alumina	17·70	...	1·25
Iron oxide	11·17	...	0·75
Water	7·65	...	—
	56·86	...	42·98

This cement has been employed for 300 years as a hydraulic mortar, and is one of the most important of its class.

Puzzolana is another tertiary earth, occurring chiefly at Puzzuoli, near Naples, as a loose, grey, or yellow-brown mass, of partly a fine-grained and partly an earthy fracture. It contains in 100 parts :—

Silicic acid	44·5
Alumina	15·0
Lime	8·8
Magnesia	4·7
Iron oxide	12·0
Potash, Soda	5·5
Water	9·2
	99·7

The oxide of iron contains small quantities of titanium. More lime must be added to form a hydraulic mortar. The masonry of the light-room of the Eddystone Lighthouse is cemented with a hydraulic mortar formed from equal parts of pulverised puzzolana and slaked lime.

Santorin derives its name from the Greek island of Santorin, where it was first found. It is, similarly to trass, a volcanic formation, and, according to G. Feichtinger (1870), consists of a mixture of cement and sand, the latter containing large quantities of pumice-stone. It is not largely employed as a cement, on account of the difficulty of separating the true cement from the accompanying sand.

Puzzolane Cements.—Under this name, or that of Victoria "cement," there are sold mixtures of finely ground slag and of lime slacked to a powder. This mixture, if kept sufficiently moist, sets slowly and becomes moderately hard. Frost has a destructive action upon recent slag cement structures, so that they are not admissible below 0°. For the first fortnight such structures should be kept uniformly moist. It is better suited for constructions under water. A further bad property of slag cements is their tendency to crack, which can be combated only by grinding the slags less finely. A

* It is also found at Ardwick, near Manchester.—[EDITOR.]

pure slag cement cannot oppose any satisfactory resistance to external mechanical action. In all probability it will not acquire importance for constructions in the air which are exposed to wear and tear. Its low initial hardness—which it shares with all puzzolanes, natural or artificial—is another defect.

Concrete.—The mention of concrete, so largely used in England, where a good weathering mortar is required, must be included in that of cements. Concrete is a mixture of ordinary mortar with stones, grit, broken brick, tiles, &c. To the concrete is generally added lime, and then the whole mixed with two or three times the quantity of fine sand. Pasely tells us that a better product may be obtained with 1 part of freshly burnt lime, in pieces not larger than the fist, $3\frac{1}{2}$ parts of sharp river-sand, and 1·5 part of water, the whole being well mixed. The bricklayer prefers to mix the dry materials and then add water, the concrete in this manner taking a longer time to harden, and admitting of greater care being taken to fill all interstices. The several uses of concrete are too well known to need mention. The employment of unslaked lime in the preparation of concrete was first introduced by Mr. Smirke, of London, to whom also its employment as a foundation to brickwork is mainly due.

Mixed Cements.—We have already mentioned that for some years a number of manufacturers and dealers have begun adding ground slags to the finished cement, under pretence of improving it. A good Portland cement cannot be improved by such additions. The admixture of slag with Portland cement, like that of heavy spar and gypsum to painters' colours, is therefore a fraud on the purchaser, and consequently to be condemned.

SECTION VI.

ARTICLES OF FOOD AND CONSUMPTION.

STARCH AND DEXTRINE.

The starch granule is an organised tissue, consisting essentially of starch with water, a little sugar, dextrine, &c. Its composition corresponds to the formula $C_6H_{10}O_5$, or, according to Mylius, $C_{24}H_{40}O_{20}$, or according to Nägeli, $C_{36}H_{62}O_{31}$. According to Dafert, starch consists of bodies which are not mutually homogeneous (starch-cellulose, granulose, dextrine), a little sugar, proteine compounds, amides, fat, and ash. He therefore considers it idle to discuss the formula of starch, since it is a mere mixture.

The starch granule consists of numerous layers, which generally contain the more water the further we proceed inwards. The innermost part is generally a hollow, filled with air, around which the layers seem to be arranged. As a rule, the thickest parts of all the layers are turned in the same direction. If they are equally thick in all directions, the granules are globular; if they are thicker in the equatorial zone, the granule has a lenticular shape. On microscopic examination the limits of the layers appear as lines, more or less distinct, running round the central cavity. Its specific gravity = 1·53. Iodine water colours starch blue, and the starch iodide formed has, according to Bondonneau, the formula $(C_6H_{10}O_5)_3I$, or according to Mylius,

$$(C_{24}H_{40}O_{20}I)_4IH.$$

Payen gives the largest dimension of the granules as 0·001 millimetre; from his researches we gain also the following examples:—

Starch granules from hard potatoes	185
,, ,, ,, ordinary potatoes	140
,, ,, ,, *Maranta indica*	140
,, ,, ,, beans	74
,, ,, ,, sago palm	70
,, ,, ,, Iceland moss	67
,, ,, ,, peas	50
,, ,, ,, wheat	50
,, ,, ,, Indian corn	50

Fig. 464 shows, according to Schleiden, granules of potato starch, and Fig. 465 of wheat starch. The potato has a larger granule, and sometimes gives a finer powder than wheat.

Nature of Starch.—Ordinary starch contains in its dry state nearly 18 per cent. water, and in this state has a tendency to form itself into globules; it has been proved that, exposed to a damp atmosphere, it absorbs 33·5 per cent. water. Starch is insoluble in cold water, alcohol, ether, and oil. At a temperature of 160° starch yields dextrine. Starch mixed with twelve to fifteen times its quantity of warm water at a temperature of 55° varies little in substance; at a temperature of 55° to 58° it begins to change, the higher temperature making the fluid thicker. Lippmann says that potato starch is affected at 62·5°, wheat starch at 67·5°. When boiled the granules burst and form

a gelatinous mass, which, largely diluted with water, can be made of a consistence to be filtered through paper, and, when allowed to cool, sets in a jelly. A stiffer paste, according to J. Wiesner (1868), is made from Indian corn than from the potato or

Fig. 464.

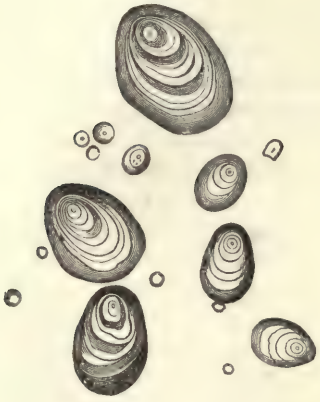


Fig. 465.



wheat. The longer the starch is boiled the stiffer the paste becomes, 1 part of starch separating in 50 parts water, and, upon cooling, setting into paste of a blue or violet hue.

Alkalies and dilute acids, with lime, tend to re-form the granules; when boiled with 2 per mille of oxalic acid, starch loses its consistence, becoming thin, and changing into a soluble substance called *dextrine*. Starch treated with almost any dilute acid, or with diastase obtained from an infusion of malt, at the proper temperature is converted into dextrine, forming a liquid which after a few hours' standing can be made into sugar. Starch is soluble in the cold in concentrated nitric acid; water dropped into this solution precipitates the granules as an explosive combination. Under the name of *xylodine*, or white gunpowder, this combination has lately been employed for pyrotechnical experiments. By boiling starch with concentrated nitric acid, a formation of oxalic acid is obtained, evolving nitrous vapours. Starch paste, upon exposure to the atmosphere, becomes sour, forming lactic acid.

In the determination of starch in raw materials, it must be considered that for the textile arts and for domestic uses only the actual starch must be considered, and sugar, if present, must be estimated separately. For brewery purposes the sugar is determined along with the starch. For the spirit manufacture it must be remembered that the sugar present is destroyed by the high pressure, whilst other substances are converted into carbohydrates capable of fermentation.

For the two former purposes, according to Reinke, 3 grammes of the sample, ground as finely as possible, are heated to boiling with 50 c.c. of water, cooled down to 62·5°, and mixed with 0·05 gramme of diastase prepared according to Lintner. Saccharification is allowed to proceed for an hour at the same temperature. The mixture is then diluted with water, cooled, and made up to 250 c.c. 200 c.c. are then inverted with 15 c.c. hydrochloric acid (of sp. gr. 1·125) at a boiling heat for two and a half hours in an Erlenmeyer flask with a reflux condenser, almost entirely neutralised with soda-lye, made up to 500 c.c., and 25 c.c. are taken for reduction with Fehling's solution. The dextrose is calculated from the reduced copper according to Allihn's tables. 100 dextrose = 90 starch.

For distillery purposes 3 grammes of the finely ground sample are stirred up with

25 c.c. of lactic acid at 1 per cent. and 30 c.c. of water heated for two and a half hours in Soxhlet's autoclave at a pressure of $3\frac{1}{2}$ atmospheres, then mixed with 50 c.c. hot water, when cold made up to 250 c.c., and filtered; 200 c.c. of the filtrate are inverted as above and used for the determination of dextrose.

Sources of Starch.—But few vegetables yield starch in large quantities; the potato yields 20 per cent.; wheat, 55 to 65 per cent.; rice, 70 to 73 per cent.; and the roots of *Jatropha Manihot* and *Maranta arundinacea*, palm pith, and the *Canna coccinea*, similar quantities. In Germany starch is prepared only from potatoes, rice, and wheat, the latter yielding a greater quantity of gum, and potato starch being thinner and not so gelatinous.

Starch from Potatoes.—Potatoes form an important material in the manufacture of starch; their constitution is as follows:—

	Newly dug Potatoes.		Potatoes dried at 100°.
Water . . .	75·1	...	—
Albumen . . .	2·3	...	9·6
Fatty matter .	0·2	...	0·8
Cellulose . .	0·4	...	1·7
Salts . . .	1·0	...	4·1
Starch . . .	21·0	...	83·8
	100·0		100·0

They contain 28 per cent. dry substance, or 23 per cent. insoluble substance, and 77 per cent. sap. The starch found in potatoes is of cellular construction; the cell walls require breaking up to fit it for manufacture. Fig. 466 shows, according to Schleiden, a fine specimen of a healthy potato under the microscope. On the outside of the potato a layer of flat, pressed, brown cells are found, sometimes appearing in a patch, *a*, forming the outer skin of the potato, and covering the cells, *b*, which some-

Fig. 466.

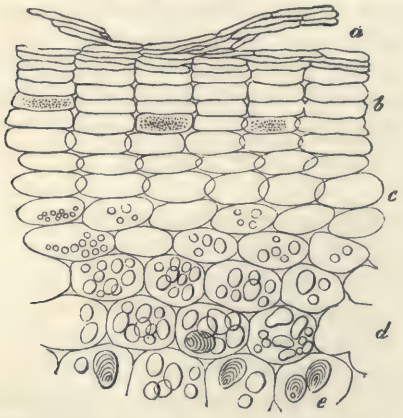
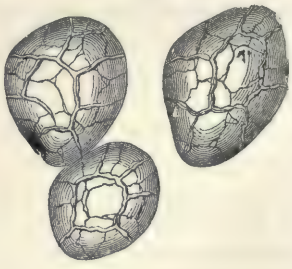


Fig. 467.



times contain a finer grain, but mostly a clear fluid. These cells become wider as they near the interior of the potato. The series of cells *c* enclose the inner cells, *d*, the pith of the potato. When the potato is dried, the cells separate from each other, as in Fig. 467, a specimen of a mealy potato. The starch granules swell in each cell, the cells uniting in reticulated streaks.

The process of manufacturing starch consists in—

1. Triturating the fresh potato.
2. Washing the starch granules from the pulp.
3. Purifying and drying the starch.

The potatoes are placed in a grinding cylinder, which formerly consisted of wood, with iron plate rollers placed half-way in water to cleanse the pulverised potato pulp. Of late grinding cylinders with saw-teeth are used (Thierry's machine). The saw-blades have short teeth, lacerating the cells to obtain the starch granules, which mere gentle washing and grinding would not effect; the cylinder revolves 600 to 700 times a minute. One cylinder, with knives 0·50 metre in length and saw-blades of 0·40 metre, can grind fourteen to fifteen batches in an hour to a pulp, which is afterwards submitted to the process of washing. A cylindrical metal sieve is generally used for separating the starch granules from the potato pulp; it contains a pair of brushes slowly rotating, whilst water is supplied to the sieve to wash the pulp, which is ground to a consistence that will admit of its readily flowing off, in order that fresh pulp may be received on the sieve. The starch granules are suspended in the water strained off, and finally settle to the bottom as a soft white powder. Laine's uninterrupted cleansing sieve is now generally used; it consists of a series of wire-work frames placed over a trough. The potato pulp flows from the grinding cylinder to a space under the cleansing sieve, from thence over two gratings, where the pulp is cleansed by a stream of water playing all over it, the granules settling down at the bottom of the trough. The granules are then crushed between steel rollers to separate the starch from the fibre. 80 to 100 cwts. potatoes can be thus prepared in a day. From the above method of preparing starch from the potato we gain the general principles of such operations. The structure of the potato is shown to be partly chemical, partly mechanical, and by destroying the latter we gain starch, which is separated after the potato pulp has been standing eight days, when it becomes a white pasty mass containing starch. This is placed in a coarse sieve, which retains a greater part of the fibre, another finer hair sieve being used to receive the starch and finer fibre, separated from each other by means of a cleansing apparatus, which washes the fibre away, leaving the starch granules and sugar behind.

Drying the Potato Starch.—The result of the washing is a milk-like fluid, which settles at the bottom of the trough as starch; it is then mixed with fresh water and allowed to solidify into a hard substance, which is cut into pieces, poured upon a linen cloth, placed on a hurdle, with a plaster-of-Paris vessel, or a vessel containing gypsum, underneath, to dry the starch. After being filtered and left to stand for twenty-four hours, the starch dries to the thickness of 2 decimetres upon the gypsum. Of late the water has been removed by a centrifugal machine. The moist starch contains 33 per cent. water, and is called fresh starch. The average temperature of the drying-rooms is not over 60°. When the starch is dried it is broken into pieces by iron rollers. The stalk or whole starch is made by boiling to a thick paste, which is forced by machinery through a small opening into a trough, where it dries in a kind of mould.

Preparation of Wheat Starch.—According to M. O. Dempwolf (1869), the unprepared wheat contains:

Water	10·51
Ash	1·50
Gum	14·35
Starch	65·40
Fatty and woody fibre	8·24
	100·00

From the constituent parts of wheat it is seen that—

Starch, Gum, Husk	are insoluble in water.	Salts, Albumen, Dextrine	are soluble.

The first three are insoluble, the gum, however, being gradually dissolved by the lactic acid developed from the seed, while the starch and husk remain unattacked.

There are two methods of preparing wheat starch—viz.:

A. By fermentation (old method) of the—

a. Unground
β. Ground } Wheat.

B. New mode of treatment without fermentation.

The old method consists of the following operations:—

1. Fermenting the wheat.
2. Washing the starch from the mass.
3. Washing and cleansing the starch.
4. Drying the starch.

The whole wheat is soaked in water until soft. The seed is separated from the husk either by treading in sacks in a flat tub of water, or by being placed under rollers, and the pulp thinned with water to a milky fluid, in which a greater part of the starch and gum are found. After standing a day this fluid turns acid; a part of the gum becomes dissolved by the action of the lactic and acetic acids, and is taken away and replaced by fresh water, the same process being gone through until the fermentation ceases, when the starch is washed with water and dried. In the fermenting tub it forms with the water a thin, sour pulp. The time varies according to the temperature; all the gum is not separated until about twelve to thirty days. The sour water contains acetic acid, lactic acid, butyric acid, succinic acid, ammoniacal salts, and the mineral constituents of the wheat. The mass is then placed in a sack and trodden, the milky fluid being allowed to escape, leaving the husk and refuse gum behind. The milky fluid containing starch is strained through a fine hair sieve and washed with water. Another method is that of placing the milky fluid in a tub and allowing it to settle. The first layer of the sediment is fine starch, next a mixture of starch, husk, and gum, the last layer containing but little starch. In the preparation a little ultramarine blue is added during the cleansing process. Of late the centrifugal machine has been used for the purpose of drying the starch.

Preparing Wheat Starch without Fermenting.—According to E. Martin's treatment, wheat flour is mixed with water to a paste, 100 parts flour to 40 parts water; the paste remains half to two hours to affect the gum, and is then washed in a fine wire sieve placed over a tub. The starch is found at the bottom of the tub mixed with water, and is placed in a warm spot to ferment slightly. It is dried in a mass, and goes through similar processes to the other starch, being made into stalk and powder starch, and sold in packets.

100 parts of wheat flour yield 25 per cent. of gum (*gluten, gluten granulé*), with 33 per cent. of water; the fresh gluten is mixed with a double weight of flour, the paste rolled into long strips, and ground into granules which become dry at 30° to 40°, and are afterwards sifted. The consumption of this granular gum is extensive, it being employed for food (with ordinary flour as macaroni), art purposes, and manufactures.

Constituents and Uses of Commercial Starch.—According to M. J. Wolff, the constituents of commercial starch are as follows:—

	1.	2.	3.	4.	5.	6.
Water	17·83	15·38	14·52	17·44	14·20	17·49
Gum	—	—	0·10	traces	1·84	4·96
Fibre	0·48	0·50	1·44	1·20	3·77	2·47
Ash	0.21	0·53	0·03	0·40	0·55	1·29
Starch	81·48	83·59	83·91	81·32	79·63	73·79
	100·00	100·00	100·00	100·00	100·00	100·00

No. 1 was the finest white patent starch in stalks, of a bright and crystalline appearance, made from pure potato starch; No. 2, the finest blue patent starch, potato starch coloured with ultramarine; No. 3, pure wheat powder; No. 4, fine wheat starch in pieces; No. 5, medium fine wheat starch in yellowish-white pieces; No. 6, ordinary wheat starch in greyish-yellow coarse pieces, that upon microscopic examination appear as a mixture of potato and wheat starch. Starch is used for stiffening domestic articles in washing, for stiffening paper, and extensively in the linen and cotton manufacture, in gum, syrups, sago, vermicelli, &c. It is also a basis from which we can obtain sugar. Potato starch is preferred for domestic washing, but where great stiffness is requisite, wheat starch is used, as in book-binding, &c. In wheat starch, the paste is formed of closely united gelatinous particles, which are more widely disseminated in potato starch, the latter being transparent and more suitable for stiffening fine linen, ironing smoother, and not sticking. Wheat starch will keep fresh upon exposure to the atmosphere longer than potato starch, the latter turning sour after a day's standing.

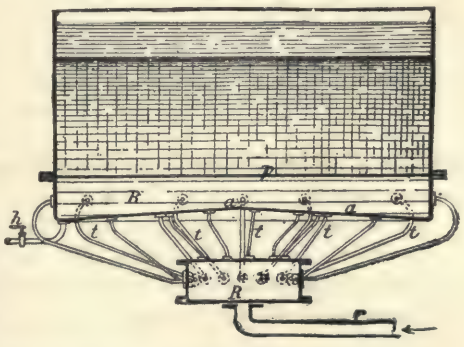
According to C. Wiesner (1868), maize starch possesses the highest, wheat the next, and potato starch the most inferior stiffening qualities. Maize and wheat are considered the best for forming a smooth, equal paste. Sugar can be prepared from starch by means of the active principle of malt—diastase. From this sugar, again, brandy and spirits can be distilled. According to the researches of Lüdersdorff:

100 pounds of potato starch need 25·5 pounds of dry malt, and
100 „ wheat „ „ 90·5 „ „
to effect the full conversion of the starch into sugar.

Rice Starch, Maize Starch, Chestnut Starch, Cassava Starch, Arrowroot.—Rice starch is largely manufactured in England, France, and Belgium. To extract the gum, rice is placed in a bath of weak soda solution—287 grammes of caustic soda to the hectolitre. After standing twenty-four hours, the rice grain becomes softened, and is then washed, ground between rollers or millstones, and placed on a sieve with brushes to retain the husk or bran. The water strained off contains the starch, which is washed, dried, and manufactured into the form required. The gum-containing alkaline lye being neutralised with sulphuric acid is fit for inferior uses. J. & J. Colman's rice starch manufacture employs 1000 workpeople, and the result of their manipulation is used as the customary washing starch, the stiffer and brighter starch for ball dresses, window hangings, and for the size in paper manufacture.

Rice Starch.—Mack treats rice in a steeping-vat with double sides (Fig. 468). Atmospheric air rushes in from all sides in such quantities that the mass is kept in a state of motion like ebullition. The rice is heaped up on the perforated false bottom, *p*, whilst the space, *B*, under the false bottom, and the free space above the rice are filled with the dilute soda-lye. The air is introduced under pressure through the tube, *r*, into the receptacle, *R*, from which it passes through many narrow pipes, *t*, into the space, *B*, and then through the false bottom, *p*, into the rice. The floor, *a*, is raised towards the centre, so that the liquid can be let off afterwards through the cock, *h*, when the rice is left half dry on the floor, *p*.

Fig. 468.



Maize Starch.—Maize is softened, ground, pressed, ground again, and finally treated with caustic alkalies. This treatment is important, as it is necessary to remove oil, mineral matter, and the nitrogenous compounds which enclose the starch. Rice starch is

separated into three qualities by a process of elutriation, which contain, according to Archbold:

	I.	II.	III.
Starch	98·5	92·88	90·33
Gluten and cellulose	—	2·38	4·25
Ash	0·3	0·60	0·65
Water	1·2	4·14	4·77

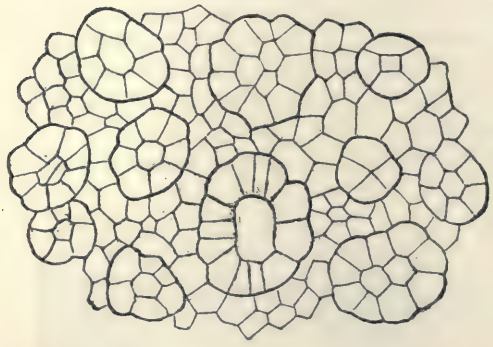
According to Tschirch, maize flour contains starch granules of two distinct forms more or less angular, almost isodiametric, and polyhedral granules often adhering together in groups of nearly the same size (Fig. 469); and rounded grains, varying much more in size (Fig. 469, m).

Fig. 469.



The starch granules of rice are almost exclusively angular (tri-, quadra-, pent-, or hexangular). Large or conglomerated masses are often found (Fig. 470). There are found in rice flour, though less commonly in starch, fragments of such conglomerates (Fig. 471). The sharpness of the angles is the most prominent characteristic of rice starch. According to Tschirch, the largest granules do not exceed 8·5 micromillim., and the smallest have a size of 4·5 to 6 micromillim.

Fig. 470.



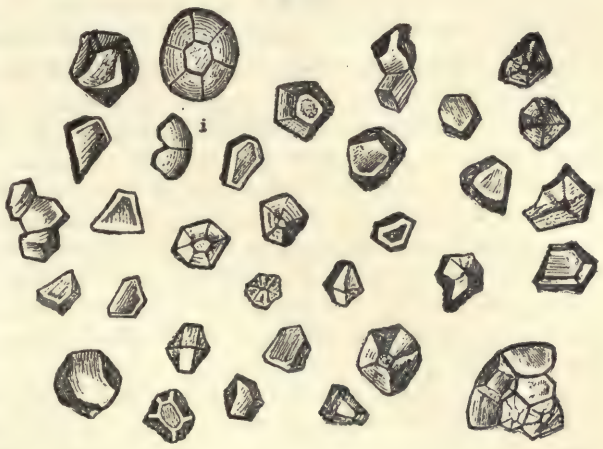
In France the *horse-chestnut* is used for the manufacture of starch. Chestnuts produce a starch possessing the evenness of potato starch with the stiffness of wheat starch. 100 parts of the fresh bitter chestnut give 19 to 20 per cent. dry starch.

Arrowroot is obtained from the *Maranta arundinacea* and *M. indica*, cultivated in the West Indies; it is very like potato starch, and is prepared in a similar manner. Cassava starch is made from the root of *Jatropha Manihot*, or *Manihot utillissima*, and *M. aipin*, largely cultivated in South America, the West Indies, and the Brazils.

Cassava is used as an article of consumption both in Europe and the Tropics. The root of the manioc is thoroughly purified from its poisonous juice, being coarsely ground to allow the sap to escape, and roasted in an earthenware vessel, the cassava forming into granules on the sides of the vessel (*Cassava sago*, or *Tapioka*), the prussic acid

contained in the root becoming volatilised. From arrowroot and the analogous roots containing a poisonous juice, arrowroot derives its name, having been used by the Indians as a poison for the tips of their arrows. Its components, according to Benzon, in 100 parts, are:—Volatile oil, 0·07 part; starch, 26 parts, 89 per cent. of the starch being obtained in a powder, while the remainder is extracted from the parenchyma by boiling water; albumen, 1·58 part; gum, 0·6 part; calcium chloride, 0·25; insoluble fibrin, 6 parts; and water, 65·5 parts. It is known in commerce in several varieties—viz., Portland arrowroot, *Arum vulgare;* East India arrowroot, *Curcuma angustifolia;* Brazilian arrowroot, *Jatropha Manihot;* English arrowroot, from the starch of the potato; Tahiti arrowroot, *Tacca oceanica.*

Fig. 471.



Sago.—Sago is made from the soft central portion of the stem of the palm, *Sagus Rumphii.* According to J. Wiesner, the Guadaloupe sago is prepared from *Raphia farinifera*, and an East Indian variety from *Caryota urens.* The stem is torn to filaments and elutriated on a sieve with water. The starch obtained is then washed, dried, and sifted into a copper plate, where it remains a hard granular substance. A greater part of the common sago is manufactured from potato starch, coloured with oxide of iron or burnt sugar.

Dextrine.—Dextrine, gommeline, moist gum, starch gum, or Alsace gum, isomeric with gum arabic, and expressed by the formula $C_6H_{10}O_5$, is formed by boiling starch with a small quantity of almost any dilute acid, which thins its consistence, and converts it into a soluble substance similar to gum arabic. It is soluble in cold water, insoluble in absolute alcohol, but slightly soluble in weak spirits of wine. Dextrine derives its name from *dexter*, the right, from the action of this substance on polarised light, twisting the plane of polarisation towards the right hand. Dextrine in grape sugar is converted into dextrose by the action of dilute acids. Dextrine solution does not ferment with yeast; but a little yeast mixed with a large quantity of gelatinous starch, at a temperature of 160°, quickly liquefies it, dextrine being produced, the greater part of which, if allowed to stand, becomes converted into grape sugar. From this decomposed dextrine a cheap and largely employed substitute for gum arabic is obtained. The components of this decomposed dextrine, according to the analyses of R. Forster (1868), are:

——	1. Dextrine.	2. Opaque Starch.	3. Dark Dextrine.	4. Gommeline.	5. Old Dextrine.	6. Bright Starch.
Dextrine	72·45	70·43	63·60	59·71	49·78	5·34
Sugar	8·77	1·92	7·67	5·76	1·42	0·24
Insoluble substances .	13·14	19·97	14·50	20·64	30·80	86·47
Water	5·64	7·68	14·23	13·89	18·00	7·95
	100·00	100·00	100·00	100·00	100.00	100·00

Potato starch is preferable to wheat starch for the manufacture of this material, not only on account of its cheapness, but for its greater purity at an equivalent price.

Dextrine is prepared by—

a. Gently roasting.
b. Carefully treating with nitric acid.
c. Boiling with dilute sulphuric acid.
d. Treating with malt extract (diastase).

Preparing dextrine by means of gentle heat is an easy operation. The starch is roasted until it becomes brown-yellow in colour, in a large copper or iron plate cylinder, similar to a coffee-drum, situated on one side of the oven. Dextrine is formed at a temperature of 225° to 260°. According to Heuzé, the following is a better method:—2 kilos. of nitric acid, of 1·4 specific gravity, with 300 litres of water, are mixed with 1000 kilos. (= 20 cwts.) of starch, and boiled to form a mass, which, when exposed to the air, becomes dry. It is sometimes effected at 80°, but it becomes a paste at 100° to 110°. The starch changes into dextrine in an hour or an hour and a half at the most; it is white and soluble in water. Sulphuric, hydrochloric, and acetic acids will produce dextrine; and by the addition of water to dextrine, dextrine syrup, or gum syrup, is obtained.

Dr. Vogel gives a simple experiment to illustrate the action of dilute sulphuric acid upon starch. Nearly all kinds of writing-paper are so very largely sized with starch, that if figures or letters are traced on the paper with very dilute sulphuric acid, and then dried, the application of iodine in a dilute solution will impart a blue tinge to that portion of the paper not affected by the acid, the characters remaining white.

Dextrine is extensively used instead of gum arabic in printing wall-papers, for stiffening and glazing cards and paper, for lip-glue, surgical purposes, wines, and in the fine arts it is applied in many ways.

SUGAR.

Those carbohydrates which are comprised under the name of sugar are divided into two great groups: those which, disregarding crystalline water, have the composition $C_6H_{12}O_6$; and those which correspond to the formula $C_{12}H_{22}O_{11}$.

I. The former group includes, chiefly, dextrose (which, when it occurs naturally, should be known as grape sugar, starch sugar, &c.), levulose (fruit sugar), arabinose, cerasinose, lactose (galactose), sorbine, eucalyne, inosite, dambose, mannitose, and others.

II. To the group $C_{12}H_{22}O_{11}$ there belong saccharose (cane sugar and beet sugar), trehalose (mycose), melezitose, melitose (raffinose), maltose, galactose (or lactose, milk sugar).

The sugars of the latter group, on treatment with dilute acids, undergo inversion, *i.e.*, take up the elements of water, and are converted to equal quantities of sugars of Group I., one of which is always dextrose:

$C_{12}H_{22}O_{11}$	+	H_{20}	=	$C_6H_{12}O_6$	+	$C_6H_{12}O_6$
Saccharose	+	water	=	dextrose	+	levulose.
Trehalose	+	,,	=	,,	+	dextrose.
Melitose	+	,,	=	,,	+	eucalyn.
Maltose	+	,,	=	,,	+	dextrose.
Galactose	+	,,	=	,,	+	lactose.

The sugars of technical importance are dextrose, inverted sugar (dextrose and levulose), maltose, and saccharose.

Grape Sugar.—Grape sugar (potato sugar, starch sugar, glucose, or dextrose) is a sugar crystallisable with difficulty, occurring in a non-crystallised state as levulose or chylariose (γυλάριον, syrup) in many sweet fruits, in the vegetable kingdom, and it

forms the solid crystalline portion of honey. It may be obtained by any of the following processes :—

a. By the conversion of starch, dextrine, cane sugar, or some gums, by means of dilute acids or diastase.

b. By treating cellulose and similar vegetable matter with dilute acids.

c. By decomposing organic substances, such as amygdalin, salicin, ploridzin, populin, quercitrin, gallo-tannic acid, &c., which by treatment with dilute acids or synaptase (emulsin) are separated into grape sugar and other substances.

Grape sugar is found in the various fruits in the following quantities :*—

	Per cent.
Peach	1·57
Apricot	1·80
Plum	2·12
Raspberry	4·00
Blackberry	4·44
Strawberry	5·73
Bilberry	5·78
Currant	6·10
Plum (sweet)	6·26
Gooseberry	7·15
Cranberry	7·45 (according to Fresenius)
Pear	8·02 to 10·8 (E. Wolff)
Apple	8·37 (Fresenius)
„	7·28 to 8·04 (E. Wolff)
Sour cherry	8·77
Mulberry	9·19
Sweet cherry	10·79
Grape	14·93

Grape sugar, $C_6H_{12}O_6H_2O$, crystallises from its aqueous solution in granular, hemispherical, warty masses. It is less easily soluble in water than cane sugar, and requires $1\frac{1}{3}$ of its own weight of cold water, while in boiling water it is soluble in all proportions, forming a syrup possessing but poor sweetening qualities. There are required $2\frac{1}{2}$ times more grape sugar than cane sugar to sweeten the same volume of water. At 120° grape sugar loses its water, and has the formula $C_6H_{12}O_6$. At 140° it is converted into caramel. Heated with caustic alkalies, melassic acid is formed, together with humus-like substances. Treated with sulphuric acid, grape sugar forms sulpho-saccharic acid ; and with common salt, a soluble compound of sweetish saline taste. With caustic potash in excess, a grape-sugar solution, when heated to the boiling-point, reduces the hydrate of copper oxide to suboxide, silver oxide to metallic silver, and gold chloride to metallic gold. A mixture of potassium ferricyanide and potash with the aid of heat decomposes grape sugar, and discharges the original yellow colour of the fluid. Under the influence of a ferment grape sugar suffers many changes, the product varying with the ferment and method of treatment employed. Beer yeast decomposes grape sugar into alcohol and carbonic acid.

100 kilos. of grape sugar give :

Alcohol	51·11
Carbonic acid	48·89

There are also found, under certain conditions of temperature and concentration, the homologues of alcohol—viz., propylic alcohol, butylic alcohol, and amylic alcohol ; and under all conditions glycerine and small quantities of succinic and lactic acids. When fermentation is effected in the presence of alkaline reagents, lactic acid is

* The sweetness of a fruit does not depend simply on the quantity of sugar. The proportion and the kind of acid, and the presence or absence of gum, have to be considered.—[EDITOR.]

formed without any disengagement of gas. Ordinarily the formation of lactic acid is merely a stage in the process of conversion, the lactic acid decomposing into butyric and acetic acids, with development of hydrogen. Under certain conditions mannite may be prepared from grape sugar; several other gum-like substances may also be obtained. If to a grape-sugar solution a small quantity of caseine and calcium carbonate be added, and the mixture submitted to a temperature of 90°, calcium butyrate will be thrown down after fermentation, carbonic and hydrogen gases being continuously evolved.

Preparation of Grape Sugar.—Grape sugar may be prepared from—

a. Grapes.
b. Starch.
c. Wood and similar vegetable substances.

When grape sugar is prepared from the grape, the juice of the white grape is preferred, and set aside to clear. The cleared must is heated to the boiling-point with pieces of marble, chalk (not with burnt lime), or witherite (barium carbonate), to neutralise a portion of the tartaric acid. It is then allowed to stand for twenty-four hours, and during this time the insoluble salts of lime are deposited. The must is now cleared with ox blood, in the proportion of 2 to 3 litres of blood to 100 litres of must, and next evaporated to 41° Tw. After remaining a short time in a tub to clear, the impurities are removed, and the must again evaporated—this time to 57° Tw. By these means a syrup is produced, from which the grape sugar can be immediately obtained. The syrup is concentrated by boiling, and run into crystallising vessels, where after three to four weeks the sugar crystallises out; it is separated from the non-crystallised chylariose in a centrifugal machine. For experimental purposes the crystals may be separated by placing the concentrated syrup on a heated porcelain or glass plate.

1000 parts by weight of grapes give:

Must	800
Syrup	200
Raw grape sugar . .	140
Pure grape sugar . .	60–70

The preparation of grape sugar from starch is an important branch of the sugar-boiler's art. Dilute sulphuric acid and the fecula of potato starch are the active agents. The principal processes are the following:—

a. The Boiling of the Starch-meal with Dilute Sulphuric Acid is effected on a small scale in leaden pans, but in an extensive preparation iron pans are employed. The requisite quantity of water is first heated to the boiling-point, and to this is added the sulphuric acid diluted with 3 parts by weight of water. The starch is also previously brought, by the addition of water, to a milky consistency. The liquids so prepared are mixed, and the boiling continued until all the starch is converted into sugar. An intermediate stage, not usually noticed by the manufacturer, is the conversion of the starch into dextrine, which in its turn suffers conversion into grape sugar. The entire conversion of the dextrine into grape sugar cannot be ascertained with certainty by the iodine test, as sometimes a purple-red tint is produced, while in others there is no change. The most reliable test is that with alcohol, founded on the known insolubility of dextrine in an alcoholic menstruum. To 1 part of the solution to be tested there are added 6 parts of absolute alcohol: if no precipitate is thrown down there is no dextrine remaining, and the conversion has been entire. The proportions of the materials are generally to 100 kilos. of starch-meal—2 kilos. of ordinary sulphuric acid of 130° Tw. and 300 to 400 litres of water.

The conversion of the starch into grape sugar is hastened by the addition of a small quantity of nitric acid.

b. The Separation of the Sulphuric Acid from the Sugar Solution is a most important operation, for the colour, purity, and flavour all depend upon success in this stage of the process. The acid is neutralised by baryta or by lime, with either of which it forms a precipitate, deposited at the bottom of the neutralisation vessels, and leaving a clear supernatant syrup. The baryta can be employed as carbonate (witherite), and is without doubt the better neutralising agent, barium sulphate being very insoluble. Lime, although ordinarily used, forms with the sulphuric acid a sulphate (gypsum) that is not perfectly insoluble in water. It can be employed either as marble, chalk, or caustic lime. The neutralisation is completed in the boiling-pan while the sugar solution is still hot. For every kilo. of sulphuric acid so much pulverised marble is required as the varying strength of the acid may demand. After the addition of the marble powder, and when the effervescence has subsided, the liquid must be tested with litmus-paper, or, better, with tincture of litmus; if the sugar solution be neutralised when at 41° Tw. density, the following evaporation will concentrate even the smallest quantity of sulphuric acid which may have remained, and render another neutralisation necessary. To ensure perfect neutralisation it is useful to add an excess of barium carbonate in the proportion of 250 to 500 grammes to every 10 kilos. of sulphuric acid.

c. Evaporating and Purifying the Sugar Solution.—This part of the process is accomplished first in a copper pan over a slow fire, or, better, by heating with steam. The impurities separate and are absorbed in the scum, which is removed by means of ladles. The evaporation is continued until the syrup marks 21° to 23° Tw., when it is passed through a filter, generally of animal charcoal. It is then removed to a large reservoir, and, if a granular sugar be desired, evaporated to 71° to 73° Tw. in flat pans, from which it is taken to be placed in the crystallising vessels. These vessels are provided at the bottom with twelve to twenty-four holes, into which wooden plugs are fitted, by removing which, when the sugar has crystallised, the molasses are removed. The crystals are dried, sifted, and either pressed into sugar-loaf forms or packed in casks. The crystallisation is effected in eight to ten days.

The manufacture of grape sugar from wood and similar vegetable substances is only of value in relation to the production of spirits, and recently as a bye-process of the manufacture of paper from wood.

Composition of Starch Sugar.—The composition of starch sugar as it occurs in commerce is very varied. During inferior seasons the marketable starch sugar may contain 50 per cent. sugar, 32·5 per cent. foreign substances, and 17·5 per cent. water. G. Schwaendler found by the analysis of various samples of the year's (1870) sugar the following percentages:

	1.	2.	3.	4.	5.
Grape sugar . .	67·5	64·0	67·2	75·8	62·2
Dextrine . . .	9·0	17·4	9·1	9·0	8·8
Water . . .	19·5	11·5	20·0	13·1	24·6
Foreign substances .	4·0	7·1	3·7	2·1	4·4
	100·0	100·0	100·0	100·0	100·0

Uses of Grape Sugar.—The sugar prepared from starch, in addition to the sugar yielded really by the grape, is largely employed in wine making and in the brewing of beer. In the latter case the grape sugar is prepared by means of diastase. That its use is extensive may be gathered from the fact that to 3 cwt. of malt 1 cwt. of potato sugar is employed. It is also employed instead of honey in confectionery, for colouring liquors and vinegars brown, in rum and cognac, beer and wines. In the latter cases it is known as *sucre-couleur*, being then a grape sugar that has been remelted, sometimes with the addition of sodium carbonate or caustic soda to deepen the colour.

Grape sugar made from maize in America is used in the manufacture of spurious honey.*

Steiner examined four kinds of starch sugar; Wagner analysed a French crystal syrup (V.) and a solid grape sugar (VI.):

——	I.	II.	III.	IV.	V.	VI.
Water	15·50	6·00	13·30	7·60	12–15	15–18
Ash	0·30	2·50	0·40	1·10		
Dextrose	45·40	26·50	76·00	—	64	64–66
Maltose	28·00	40·30	5·00	42·60		
Dextrine	9·30	15·90	—	39·80	21	18–22
Carbohydrates	1·50	7·00	5·30	8·90		
Proteines	traces	1·80	0·20			
Acid = SO_3	0·08	0·03	0·05			

Sample I., from a German factory, is white and soft; the other samples are from English factories, No. II. being obtained by treating maize with sulphuric acid under high pressure, and is tough like IV.; III. is solid.

Neubauer examined in 1875 a number of German starch sugars, and found on an average:

Fermentable sugar	61·08
Non-fermentable matter	20·54
Ash, chiefly gypsum	0·34
Water	18·04

Sieben, in 1884, found the following composition of syrupy starch sugar:—

Dextrose	21·70
Maltose	15·80
Dextrine	41·96
Water	20·10
Ash	0·30

German starch sugars are generally obtained from potato starch.

The product obtained in the United States from maize starch treated with sulphuric acid (rarely oxalic acid) has the following composition:—

	Syrup.		Solid Sugar.
Dextrose	34·30 to 42·80	...	72·00 to 73·40
Maltose	0·00 „ 19·30	...	0.00 „ 3·60
Dextrine	29·80 „ 45·30	...	4·20 „ 9·10
Water	14·20 „ 22·60	...	14·00 „ 17·60
Ash	0·32 „ 1·06	...	0·34 „ 0·75

Inverted sugar has been latterly used to some extent in the manufacture of champagne, in Gallicising wines, in confectionery, &c. It is obtained by inverting solutions of cane sugar with carbon dioxide. It is a mixture (or a compound) of dextrose and levulose.

Maltose.—The sugar obtained by the reaction of extract of malt upon starch paste forms a mass consisting of fine crystalline needles, soluble in water, of a faintly sweetish taste, and convertible into dextrose by boiling with dilute sulphuric or hydrochloric acid. In a solution of neutral copper acetate, acidulated with acetic acid, dextrose reduces red cuprous oxide on heating, whilst maltose does not. Maltose is directly and completely fermentable without previous conversion into dextrose.

According to Schulze, 100 parts of anhydrous maltose have the same reductive power as 66–67 parts dextrose. The air-dry substance contains 5 per cent. crystalline water. Its composition corresponds to the formula $C_{12}H_{22}O_{11}.H_2O$. If dried at 100°

* It would be well if the name *grape sugar* were reserved exclusively for the natural product, and if the factitious varieties were known as *starch sugar*.—[EDITOR.]

in a current of air, it has the same composition as cane sugar. According to Meissl, the specific rotatory power of maltose becomes smaller with increasing concentration and rising temperature, and, as seen by the sodium light, in a solution containing P per cent. of anhydrous maltose at T°, it may be expressed by

$$[a]D = 140{\cdot}375 - 0{\cdot}01837P - 0{\cdot}095T.$$

The rotatory power of freshly prepared solutions is less by 15 or 20 per cent. than that of such as have stood for some time. It melts below 100°. Anhydrous dextrose crystallises in the form of needles and columns, which melt at 146°.

According to Soxhlet, for obtaining maltose 2 kilos. of potato starch are made into paste with 9 litres water on the water-bath. After the paste has cooled down to 60° to 65°, an infusion of 120 to 140 grammes of air-dried malt, prepared at 40°, is stirred into the paste, and is kept at that temperature for an hour. It is then heated to a boil, and filtered whilst hot, and evaporated to a syrup in flat dishes. This syrup is then repeatedly boiled by portions with alcohol at 90 per cent. After a portion has thus been extracted once or twice, it is lixiviated with absolute alcohol. The matter thus obtained is evaporated to a syrup, and let stand in thin layers to crystallise.

Dubrunfaut attempted to produce maltose for breweries, distilleries, &c., by saccharifying maize, potatoes, &c., with extract of malt. The patent was sold for £10,000, but it has not proved successful in practice.

Cane Sugar (saccharose) is found in the sugar-cane, in maize, in the sap of several species of maple and of the birch, in the beet, the carrot, in madder-root, in pumpkins, melons, bananas, pineapples, and in several species of palm.

The Sugar-cane.—The sugar-cane, *Saccharum officinarum*, is a plant of the grass tribe; its stalk is round, knotted, and hollow, and the exterior of a greenish yellow or blue, with sometimes violet streaks. It grows from 2·6 to 6·6 metres high, and from 4 to 6 centimetres in thickness; the interior is cellular. The leaves grow to a length of 1·6 to 2 metres, and are ribbed. The plant is grown from seed, and also cultivated from cuttings.

A hectare of land yields raw sugar:—

	By 15 Months' Cultivation.	In 1 Year.
From Martinique . . .	2500 kilos. ...	2000 kilos.
„ Guadaloupe . . .	3000 „ ...	2400 „
„ Mauritius . . .	5000 „ ...	4000 „
„ Brazil	7500 „ ...	6000 „

Components of the Sugar-cane.—The sugar-cane yields the largest amount of sugar, generally 90 per cent. juice, containing, according to Péligot, 18 to 20 parts crystallised sugar. The components of sugar-cane, according to the analyses of Péligot, Dupuy, and Icery, are as follows:—Martinique (*a*); Guadaloupe (*b*); Mauritius (*c*).

	(*a*) Péligot.	(*b*) Dupuy.	(*c*) Icery.
Sugar . . .	18·0 ...	17·8 ...	20·0
Water . . .	72·1 ...	72·0 ...	69·0
Cellulose . . .	9·9 ...	9·8 ...	10·0
Salts . . .	— ...	0·4 ...	0·7—1·2

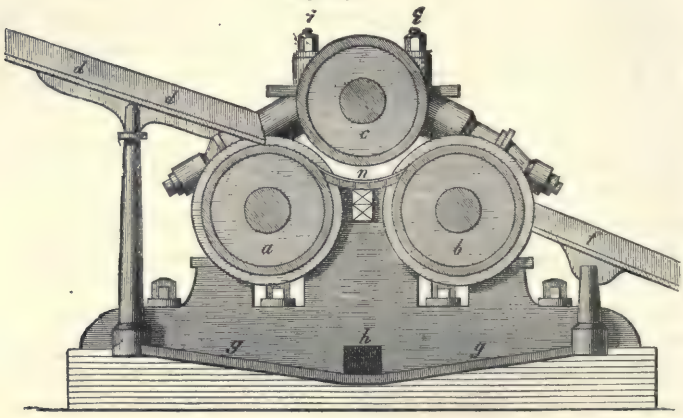
From 18 per cent. sugar found in the sugar-cane, as a rule not more than 8 per cent. crystallised sugar can be realised. The loss may be accounted for thus:—90 per cent. juice is expressed from the cane, from which only about 50 to 60 per cent. can be clarified from the straw, &c.; a fifth part is exhausted by refining; and finally two-thirds of the sugar is obtained by boiling, while the rest goes to the molasses. The 18 per cent. sugar may be realised in the following manner:—

In the refuse sometimes remains	6·0	per cent.
By skimming	2·5	„
In the molasses	3·0	„
As raw sugar	6·5	„
	18·0	„

Preparing the Raw Sugar from the Sugar-cane.—The preparation of raw sugar from the sugar-cane consists in first expressing, and then cleansing and boiling the juice.

1. *Expressing the Juice.*—The sugar-canes are crushed in a press consisting of three hollow cast-iron rollers, *a b c*, Fig. 472, placed horizontally in a cast-iron frame. By means of the screws, *i i*, the approximate distance of the rollers is adjusted. One roller is half as large as the others, and is moved by three cogged wheels fitted on to the axis of the rollers. The sugar-canes are transferred from the slate gutter, *d d*, to the rollers, *a c*, which press them a little, and from thence they are carried over the arched plate, *n*, to the rollers, *c b*. The pressed sugar-canes fall over the gutter, *f*, the expressed juice collecting in *g g*, and running off through *h*. The middle roller is termed the king roller; the side cylinders are individually the side roller and macasse.

Fig. 472.



Latterly the diffusion-process has been introduced in the cane-sugar works, to the great improvement of the yield.*

2. *Refining and Boiling the Juice.*—The expressed juice is removed to the boiling house, which is fitted with five iron or copper vessels. To 15,000 litres of expressed juice 5 to 9 litres of milk of lime are added. The lime neutralises the malic and other vegetable acids, and upon boiling forms, with the albumen and the other constituents of the juice, a thick green scum, which being removed the juice is allowed to remain in two of the pans to evaporate. A fresh scum is formed on the first pan, which returns after a second or third time of removal. A juice as it issues from the press is received into the first pan, in which, by slow boiling, it becomes a thick froth, changing by rapid boiling to a clear colourless fluid; in the third and fourth pans the liquid becomes gradually purer, until in the fifth it crystallises. The finger is dipped into the boiled juice to test its consistence, and by the length of the pendant drop, which ought to be about 3 centimetres, the thickness is ascertained. The boiled juice is placed in a large open wooden vessel of about 16 centimetres capacity, and termed the cooler, where, after standing twenty-four hours, the sugar crystallises, the cooler being provided with a double perforated bottom to allow the molasses to escape, leaving the crystals behind. After standing five or six weeks, the molasses dries into a mass commonly known as moist, raw, or Muscovado sugar. The molasses passes into a cistern placed underneath the cooler, capable of con-

* If the further improvements devised by Prof. Galloway are introduced, the sugar-cane need fear no competition in a fair market.

taining 15,000 to 20,000 litres of juice, and after standing fourteen days is ready for the market. In the French and English colonies sugar is exported in chests covered with fire-clay under the name of chest or tub sugar.

Varieties of Sugar.—European commerce deals with the following kinds of raw sugar:—

1. West Indian—Cuba, San Domingo or Haiti, Jamaica, Porto Rico, Martinique, Guadaloupe, St. Croix, St. Thomas, Havanna.

2. American—Rio Janeiro, Bahia, Surinam, Pernambuco.

3. East Indian—Java, Manilla, Bengal, Mauritius, Bourbon, Cochin China, Siam, Canton.

Of late there has been a distinction between sugar cultivated by slave and that by free labour: the latter comes from Jamaica, Barbadoes, Demerara, Antigua, Trinidad, Dominica; the former from Cuba, Havanna, Brazil, St. Croix, and Porto Rico.

The mode of manufacture varies according to the nature of the foreign substances that always form part of the constituents of sugar, such as water, fibre, gluten, sand or earth, soluble mineral salts, acetic and other acids, all of which must be destroyed before the sugar can be refined. According to Renner we have in the following sugars from:—

	Java.		Havanna.		Surinam.	In Sugar Candy.
Raw sugar . .	98·6—83·1	...	97·0—87·3	...	92·3—85·4	... 99·6
Slime sugar . .	5·5— 0·3	...	3·7— 0·9	...	4·4— 1·6	... 0·1
Water . . .	6·1— 0·3	...	3·5— 0·9	...	6·3— 3·6	... 0·2
Ash	2·1— 0·2	...	1·4— 0·0	...	2·0— 1·2	... 0·1
Caramel, gum, vegetable acids, &c.	3·5— 0·5	...	4·5— 0·4	...	2·1— 1·1	... —

Molasses.—The production of molasses is due to the long-continued heating of the cane juice, but the quality varies according to the nature and culture of the sugar-canes, the heat of the season, &c. By chemical treatment molasses appears as a concentrated watery solution of crystallised sugar, slime sugar, with a small admixture of caramel and mineral salts. It is a dull red-brown sweet fluid used principally in the colonies for the manufacture of rum; it is soon converted to spirit, and then quickly becomes acetated. Renner gives the constituents of molasses as:—

Raw sugar	32·97	...	40·36
Slime sugar	4·30	...	7·38
Water	13·71	...	16·25
Ash	3·35	...	3·78
Caramel, gum, &c. . . .	45·65	...	32·22

Refining the Sugar.—Sugar refining consists in—

1. Dissolving and Refining.—The raw sugar is dissolved in water, and during the process of evaporation the apparatus is connected by a gutter to a reservoir, into which the sugar flows. It is then submitted to a straining apparatus, which retains the several impurities. The refined fluid is then heated in a copper pan, termed the melting pan, the water adding 30 per cent. to the weight of the sugar, and is afterwards placed in the refining pan, a vessel constructed with a double bottom. For the purpose of clearing, a mixture of albumen is added in the shape of serum of blood, or white of egg, with lime-water and sulphuric acid, an addition afterwards being made of 3 to 4 per cent. animal charcoal and ½ to 2 per cent. blood, and the whole heated to the boiling-point. The albumen coagulates and forms a fibrous scum, containing all the impurities.

2. Taylor's filtering apparatus is now much used for filtering the sugar, charcoal being employed as the purifying agent.

3. The boiling of the clear sugar in pans placed over a vacuum apparatus resembles

the previous boiling, with the exception that the fluid is rendered purer, 10 to 12 per cent. water remaining.

4. Cooling and Crystallising.—When the sugar begins to crystallise on the surface of the vacuum pan, generally at 80°, the temperature is lowered to about 50°, as too great heat at this stage of the process exercises an injurious effect upon the sugar, which now forms an amorphous mass, and is drained, washed with clean syrup, and prepared for ordinary loaf sugar. Sugar-candy is the result of slow crystallisation, the crystals by this means acquiring a larger size and more regular form.

5. The shaping of the crystallised mass into the form of a sugar-loaf is accomplished by evaporating the sugar and placing it in earthen conical moulds to solidify at a temperature of 25° to 30°. After standing ten minutes the sugar sets into form.

6. Drying the Sugar.—After standing twelve hours a green-coloured syrup is obtained from the crystalline mass, which is removed, and the crystals submitted to a centrifugal process of drying, then placed in a drying-stove at a temperature of 25°, which is gradually increased to 50°. By thus refining the raw sugar, the ordinary loaf sugar is obtained.

Beet Sugar.—Most of the sugar consumed on the European continent is obtained from a species of beet.

Species of Beet.—The vegetable known as beet-root is a large fleshy root of a plant of the species *Beta maritima*, largely cultivated in France, Belgium, Germany, and Portugal for the production of sugar. There are several varieties of the two species, the white beet being preferred on account of its yielding more sugar, and also for its purity of colour, the red beet being chiefly cultivated for culinary purposes. There is also the field beet, commonly known as the *mangold wurzel*, which was first used as provender for cattle about the end of the last century. The sugar beet has, in course of cultivation, been improved by many new methods of manuring, &c., until it yields 13 and sometimes 14 per cent. of sugar. In Germany the following varieties of beets are principally cultivated:—

1. Quedlinburg beet, a slender rose-coloured root, and very sweet; it is matured fourteen days before any other kind. 2. Silesian beet is pear-shaped, with bright green ribbed leaves: it is known as the green-ribbed beet, and does not produce so much sugar as the former. 3. Siberian beet is pear-shaped, with white-green ribbed leaves, and is known as the white-ribbed beet. It does not yield so well as the Silesian beet, although of a greater weight. 4. The French, or Belgian beet, has small leaves and a slender and spiral root, yielding sugar. 5. The Imperial beet is slender and pear-shaped, yielding much sugar. The king beet is a biennial: in the first year the root is merely developed, in the second it bears seed.

The following is a list of the countries where the beet is cultivated for sugar:—

In	According to—	Beets gathered in cwts.	The Manufacture of Suitable Beets in cwts.	Into Sugar in pounds.
Austria	Krause	104—145	88—123	770—1084
,,	Burger	169—193	143—164	1256—1560
Bohemia	Neumann	112—145	95—123	836—1160
Prussia	Lüdersdorff	146	124	1088
,,	Thaer	180	153	1336
Baden	Stölzel	120—160	102—136	896—1196
France:—				
Northern Departments	Dumas	193	168	1476
Other ,,	Dumas	124	105	924
France	Boussingault	149	127	1116

In general 140 to 160 cwts. are cultivated, cut, and cleaned per acre, there being 4 Magdeburg acres to 1 hectare, which usually yield sufficient roots for three days' work.

Chemical Constituents of the Beet.—The flesh of the beet consists of a quantity of small cells containing a clear, colourless fluid. The constituents of the sugar-beet, according to chemical analyses, are—

Water	82·7
Sugar	11·3
Cellulose	0·8
Albumen, caseine, and other bodies	1·5
Fatty matter	0·1
Organic substances, citric acid, pectin and pectic acid, asparagin, aspartic acid, and betain, a substance having, according to M. Scheibler, the formula $C_{15}H_{33}N_3O_6$	3·7
Organic salts, calcium, potassium, and sodium, oxalate and pectate	
Inorganic salts, potassium nitrate and sulphate, calcium and magnesium phosphate	

Near Magdeburg, where the beet is extensively cultivated, the general results give—

The greatest sugar production, as	13·3 per cent.
That from inferior beets, as	9·2 „
The average beet yielding	11·2 „

The components of the beet vary according to the time of the year; at some periods it contains more water than at others, from 82 to 84 per cent. being the average. In the autumn it does not contain slime sugar; in February and March the components intermingle, and some decrease nearly 2 per cent., as shown by the following analyses :—

	October.		February.
Woody fibre and pectin	3·49 per cent.	...	2·52 per cent.
Water	82·06 „	...	84·36 „
Sugar	12·40 „	...	10·60 „
Slime sugar	0·00 „	...	0·65 „
Mineral salts	0·75 „	...	0·63 „
Organic acid and extractives	1·30 „	...	1·24 „
	100·00	...	100·00

12½ cwts. of beet yield on an average 1 cwt. of raw sugar.

Saccharimetry.—For obtaining an average sample a piece is either dug out or rasped out from each root. The rasping machine of Bothmer consists of a double case, *A* (Figs. 473, 474, and 475), screwed to a block and enclosing the rasping disc, *C*. The roof-shaped friction-surfaces of this disc are fitted with a rasp lift, and their outer edge is toothed like a saw. The disc fixed on the axle, *D*, makes 1000 revolutions per minute, and can turn either to the right or to the left. The beets, *R*, are thrust through the opening, *E*, by means of a wooden handle, *H*, shown in section in Fig. 474. It is provided with four iron points, *s*, to hold fast the beets, which are then pressed against

Fig. 473.

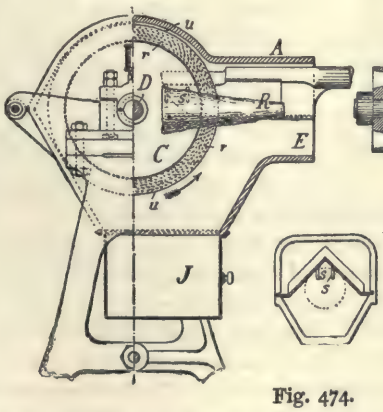


Fig. 475.

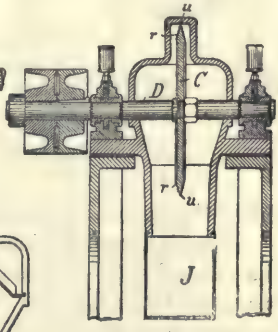
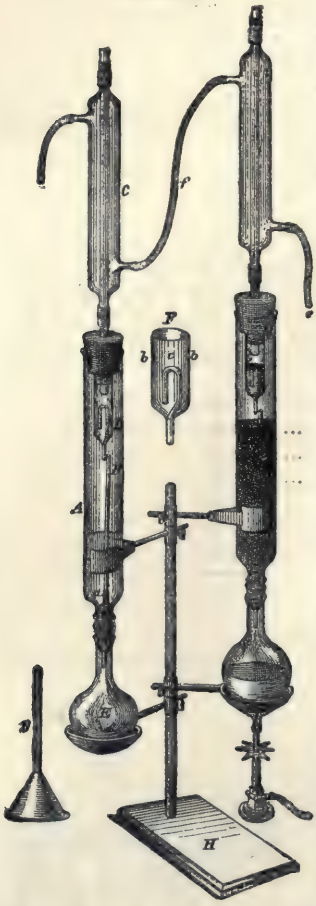


Fig. 474.

the rasper, which cuts them up lengthwise and tears them to a pulp. This pulp falls into a collecting-box, *J*, set below. The pulp thus obtained is covered with alcohol, which is then filtered off, or it is lixiviated in an extraction apparatus.

Stockbridge recommends a lixiviation apparatus, the cylinder of which, *A* (Fig. 476), is a glass tube somewhat contracted below, 32 centimetres long and 36 centimetres wide. Through its lower aperture, closed with a caoutchouc stopper, there passes a tube, *B*, ground off obliquely, 28 centimetres long and 0·8 wide, connecting the extraction cylinder with the flask, *E*, containing 250 c.c., and traversing its caoutchouc plug. The annular space between the tube, *B*, and the cylinder, *A*, is intended to receive the beet-pulp, and holds about 100 c.c. The tube, *B*, has an aperture, *a*, just above the caoutchouc plug, and round it at this point is wrapped a piece of wire gauze, so that when there is liquid in the pulp it can run off clear and without difficulty into the flask. The upper end of the cylinder is closed with a caoutchouc stopper, through which passes the pipe of the reflux condenser, *c*. When the contents of the flask are boiled, the vapours pass through the ascending tube, *B*, into the cylinder, *A*, and the contents are heated almost to the boiling-point of alcohol, whilst the alcohol is partly liquefied, saturates the beet-paste, and returns partly through the aperture, *a*, into the flask, *E*. The alcoholic vapour condensed in *A* passes into the cooler, *C*, where it is liquefied, and drops back into the apparatus. In order to effect a sudden and complete saturation of the beet-pulp, the apparatus, *D* and *F*, is secured to the lower end of the cooling tube by means of a caoutchouc stopper. This apparatus is a tube, 2·5 centimetres wide and 7·5 centimetres long, closed below, and having above two holes, *b*, through which the vapours arrive in the cooling tube. The alcohol liquefied in the cooler is thus not permitted to drop upon the contents of the extractor, *A*, but it is compelled to collect in *D*. Through the bottom of *D* there passes a tube, *c*, bent above like a syphon nearly to the bottom of the vessel, whereby, as soon as alcohol enough to cover the bend of the tube has collected in the vessel, the syphon begins to work, and all the alcohol which has collected is poured upon the beet-pulp. Thus the entire surface is covered; the saccharine juice is rapidly displaced, and flows through the wire-gauze and the hole in the inner tube into the flask. This process repeats itself hourly, from twelve to thirty times, according to the intensity of the heat.

Fig. 476.



For the determination of the sugar, about 80 grammes of beet-pulp are placed in the extraction tube by means of the funnel, *g*; about 140 c.c. of alcohol at 95 per cent. are poured into the flask, the sand-bath is heated, and the pulp is satisfactorily lixiviated in about an hour and a half. The flask, which contains the total sugar of the sample, is removed from the extractor; its contents are placed in a 200 c.c. flask, rinsed with alcohol, and 5 per cent. basic lead acetate is added. The flask is now filled with 95 per cent. alcohol up to the mark; the liquid is filtered and polarised in the ordinary manner.

Extraction of Sugar from the Root.—The preparation of sugar from the beet consists in the following operations :—

1. Washing and cleansing the beet.
2. Separating the juice from the root.
 - *a.* The root is ground to a pulp and subjected to hydraulic pressure.
 - *β.* The juice is extracted from the pulp by means of a centrifugal machine.
 - *γ.* According to Schützenbach, after maceration the juice is separated from the pulp by water.
 - *δ.* The root is cut into thin slices and placed in a vessel (diffusion apparatus), with water at a certain temperature.
3. Refining the juice with lime, and removing the lime with carbonic acid.
4. Filtering the juice through charcoal.
5. Boiling the refined juice for crystallisation.
6. The manufacture of raw and refined sugar.
 - *a.* Raw or moist sugar.
 - *β.* Refined or loaf sugar.

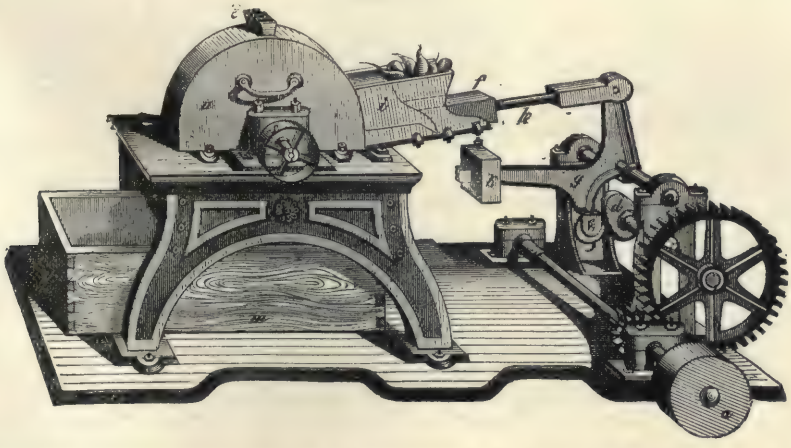
1. *Washing and Cleansing the Beet.*—The beet when newly dug requires washing and cleansing, which takes 10 and sometimes 20 per cent. from the weight of the root. Champonnois's washing machine is, perhaps, the most successful. It consists of revolving drums of open iron- or wood-work, placed in a trough supplied with water, the drums making 8 to 40 revolutions in a minute. The beets, cleansed from all impurities, and washed, are cut and submitted to elutriation on a sieve. From 1000 to 1200 cwts. beets can be prepared per day of twenty hours with 2-horse power; the length of the washing-drum being from 3·1 to 4 metres with a diameter of 1 metre, the drum making from 30 to 40 revolutions per minute.

2. *Separating the Juice from the Root.*—There are two methods of effecting this: the first by grinding the root to a pulp, and then removing the juice by—

- *a.* Pressing.
- *β.* Centrifugal force.
- *γ.* Maceration.

The sugar in the beet-root is contained in the cells, which are easily opened, but require a moderate pressure to extract the juice containing the sugar. A hand-grinding machine is sometimes found sufficient for this purpose; but Thierry's crushing machine, shown in the following illustration (Fig. 477), is generally used.

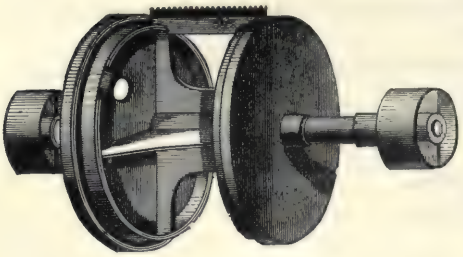
Fig. 477.



The grinding cylinder (Fig. 478) is 0·5 to 0·6 metre in length, and 0·8 to 1·0 metre in diameter, the periphery being set with 250 saw-blades. *t* (Fig. 477) is a funnel to admit water; *i* the trough into which the roots are placed; *m* the cistern to

receive the pulp. The motive power gears with *a* and *s*; and the motion of the axis of *a* is by means of the pinion, *b*, communicated to the eccentric, *d*, and friction roller, *e*, thence by the arm, *g*, and connecting-rod, *h*, to the plunger, *f*, which presses the roots against the edges of the saw-blades concealed by the case, *u*, the pressure being regulated by the weight, *k*. The cylinder revolves 1000 to 1200 times a minute, reducing from 800 to 1000 cwts. of beets to pulp in twenty hours. The water from *t* is necessary, that the pulp may be ground to a finer consistence.

Fig. 478.



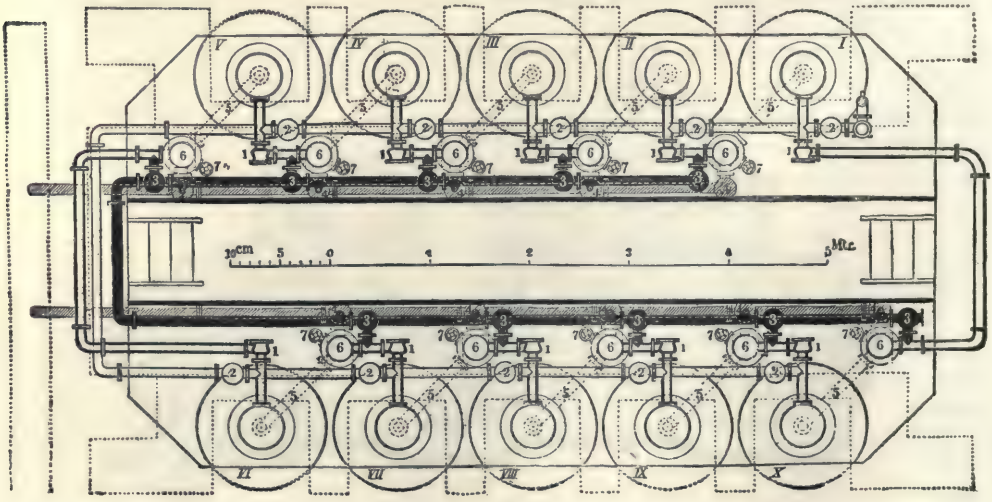
The juice is obtained by pressing the pulp by means of a stone or iron roller through a series of linen cloths. But in the French manufactories the hydraulic or Bramah press is most generally adopted. The pulp is placed in sacks or bags between iron plates, and subjected to a pressure of 500 to 600 lbs. The expressed juice flows from the bed-plate into a pipe, which conducts it to a receptacle. 100 cwts. of beet, with a pressed residue of 18 per cent., yield 82 per cent. good juice.

The production of juice from the pulp by pressure is effected either by the hydraulic press, the roller press, or the filter press. But pressure, the centrifugal process, and maceration have been almost entirely superseded in Germany by *diffusion*, which is a modification of maceration depending upon dialysis.

The roots are cut up into slices of about 1 millimetre in thickness, and digested with pure water at 50° in closed iron cylinders. The sugary juice passes through the walls of the cells and mixes with the water, whilst water enters the cells, and certain non-saccharine substances remain behind. Hence the sugary solution is tolerably pure.

The vessels used for diffusion are mostly upright iron cylinders, with flat or arched bottoms, having a large opening, capable of being tightly closed, for receiving

Fig. 479.



the slices. A number of such diffusers connected together is called a battery. In order to keep the contents at the required temperature of 50°, there is in each diffuser a copper worm lying at the bottom heated by steam. The vessels are con-

nected in such a manner by means of pipes that the same portion of liquid can be driven through the entire battery. The driving power is the hydrostatic pressure of a cistern placed 6 to 9 metres high.

A diffusion-battery, with 10 vessels and juice-heaters, is shown in ground plan,

Fig. 480.

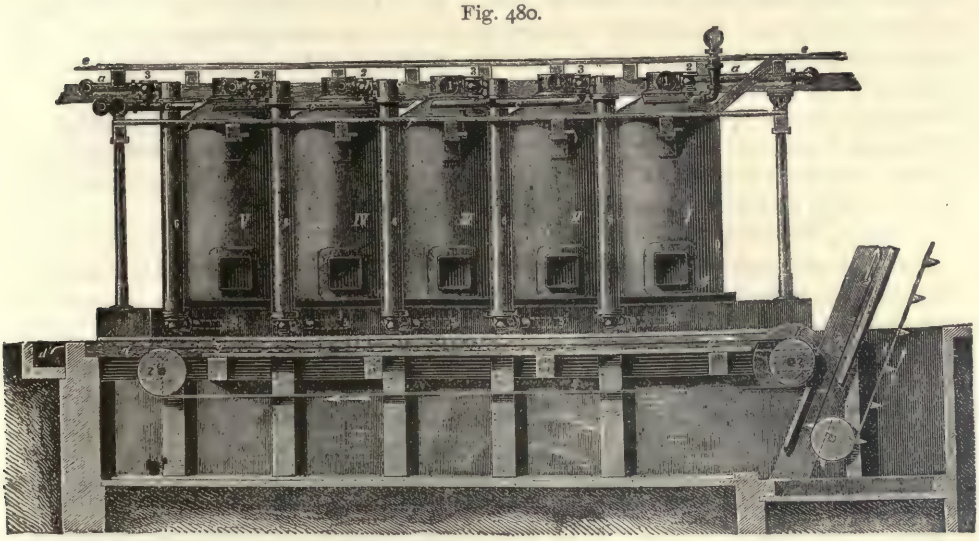
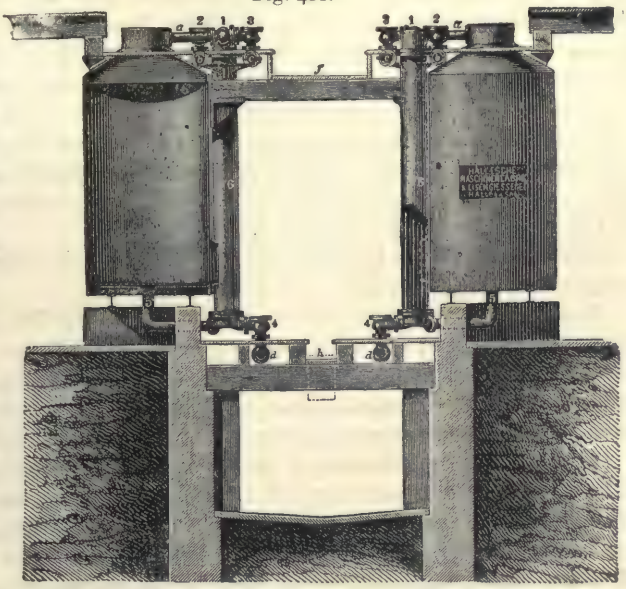


Fig. 479; in longitudinal section, Fig. 480; and in cross section, Fig. 481. From the bottom of each diffuser, *I* to *X*, passes the outflow pipe 5, and opens into the lower part of the juice-heater, where it is divided into the seven heating-pipes. At the head-end of each juice-heater is a tube, bent at right angles, the overflower, *a*, Fig. 481, which connects the juice-heater with the next following diffuser. At the bend the overflower has a horizontal valve, *I*. The form of the overflower appears from the ground plan, Fig. 479. Its entrance into the neck of the diffusers is shown in Fig. 481.

Fig. 481.



The connection of the opposite vessels, *V* and *VI*, as well as *X* and *I*, is effected so that the juice-heater is to the right of the diffuser, *V*. The overflow pipe branching off from this is considerably prolonged, and makes three bends at right angles before it opens into the vessel *VI*. The valve, *I*, of the overflower lies exactly in front of diffuser *VI*. In the same manner *X* is connected with *I*. The juice-heater stands on the right of *X*; the prolonged overflow pipe makes three knee-shaped bends before it enters the neck of diffuser *I*. The valve of the diffuser

lies straight before the neck of *I*. Close below the overflow-pipe is the water-pipe, *b*, and the pipe leading to the purifying pans, both in the same plane. To render both visible in Fig. 480, the water-pipe is drawn as if broken away in some places. The water-piping lies nearest the diffusers; it begins at *I*, and arrives there from an elevated cistern. It passes along the diffusers *I* to *V*, turns round, passes along *VI* to *X*, and ends at diffuser *X*. The purifying pan-pipe begins near the juice-heater of vessel *I*, passes from *I* to *V*, turns round, goes from *VI* to *X*, and is here prolonged to the purifying pan by a piece not shown in the drawing. The water-main has in front of every diffuser an upright valve, *II*, by means of which it is possible to establish or interrupt the connection with each diffuser. To effect the connection, a short piece of piping branches off from the main and passes into the limb of the knee-shaped overflower, which enters the diffusion vessel.

In a similar manner, the piping to the purifying pans is connected with each vessel, but with the difference that, while these are connected with the lower part of the diffusers, the water-main is connected with the upper part, as the movement of the juices has to take place in such a manner that the water enters above and displaces the juice below, causes it to pass through the next juice-heater, and passes it then either to the next following vessel or to the purifying pan.

For carrying off the water from the slicings, there are used the two pipes, *d* (Fig. 479), at the front of the juice-heaters. One of these lies in front of *I* to *V*, beginning at *I* and ending near *V*, in an open channel, *d'*. The second pipe begins near *X* and ends near *VI*, in the same channel (Figs. 480 and 481). The pipes for the slicing water are connected with the lower end of the juice-heaters by short pipes, which can be closed tightly by the valves 4. The juice-heaters are heated by the steam which enters their jackets from above at 7.

The upper man-holes of the diffusers are easily accessible from the platform, *e*, which runs along both series; a second, supported by the cross-beams, *f*, is between the two series of diffusers rather lower than *e*, so as to give access to the valves 1, 2, 3. A third, *g*, is fixed below the valves 4. From here the exhausted slicings are removed by a mechanical arrangement. For this purpose there is in the middle a sunk channel, *h*, at the bottom of which an endless web moves in the direction of the arrows. It is wrapped round the tension rollers, *i i'*, of which *i* is put in motion by a driving band at the side. The slicings drawn out of the man-holes fall at first upon the platform, *g*, and are swept into the channel, *h*, where they are carried along by the endless web, and on arriving at the roller, *i*, they fall upon a movement, *l*, in order to be taken up by the little boxes, *n*, and conveyed further.

Diffusion apparatus in which the slicings are carried along continuously to meet the water or the juice have not yet met with approval.

The advantages of the diffusion process are:—(1) The production of a purer juice, more easily worked; (2) a better cattle food; (3) diffusion allows of a more complete extraction of the sugar than any other method; (4) considerable economy of mechanical power; (5) the press-cloths are dispensed with; (6) labour is economised; (7) the juice is more concentrated; (8) the cost of the installation is much reduced.

Composition and Treatment of the Juice.—The juice, after being expressed from the pulp, if allowed to remain exposed to the action of the air, throws down a dark flaky precipitate. The more free acids the juice contains the lighter will be the colour of the precipitate, and the juice will appear of a brown-red. The juice is not only a solution of sugar, but contains the soluble constituents of the beet, in which nitrogenous and mineral substances are very prominent. Sugar under fermentation forms lactic acid and other products; but it is separated from all the impurities and refined into crystals. The usual method of refining is to boil the juice rapidly in copper refining vessels constructed with double bottoms. The rapid boiling separates the coagulated

juice, whilst the free acid is neutralised by the introduction of dilute milk of lime. The lime also serves to separate the nitrogenous substances of the juice, and enters into a combination with a small portion of the sugar, forming a sugar-lime or calcium saccharate. Lime, too, throws down from their salts iron protoxide and magnesia, while potash and soda are set free. The quantity of lime added depends upon the condition of the root. As a rule, to 100 lbs. of juice 1 to 2 lbs. of lime are added, or to 2 cwts. of roots 1 lb. of lime. The insoluble combinations of lime are separated from the juice as a slime by filtering in a filtering-press.

3. *De-liming or Saturating the Juice with Carbonic Acid.*—The clear juice is by no means a pure sugar solution, but contains besides free sugar, sugar-lime, free potash, and soda, sometimes ammonia, and a small quantity of nitrogenous organic substances, decomposed by the free alkalies, ammonia being largely developed by their evaporation. The juice also contains various organic acids (as aspartic acid) and alkaline salts (as potassium sulphate and nitrate). The decomposition of the sugar-lime effects the removal of the extraneous substances from the juice. The physical method of purifying the juice is by filtering it through animal charcoal, while the chemical method is effected by means of carbonic acid. The use of carbonic acid was first recommended by Barruel, of Paris, in 1811, and later by Kuhlmann, Schatten, and Michaëlis. The latter obtained the gas from the action of sulphuric acid upon chalk, or, better, upon magnesite; the former employed the gas resulting from the combustion of charcoal or coke. Lately, Ozouf has prepared carbonic gas by heating sodium bi-carbonate. In the German manufactories the decomposition of the sugar-lime is effected in a Kleeberger's pan (Fig. 482). This apparatus consists of a cast-iron cistern, *B*, to contain the juice. The carbonic acid, having been washed in pure

Fig. 482.

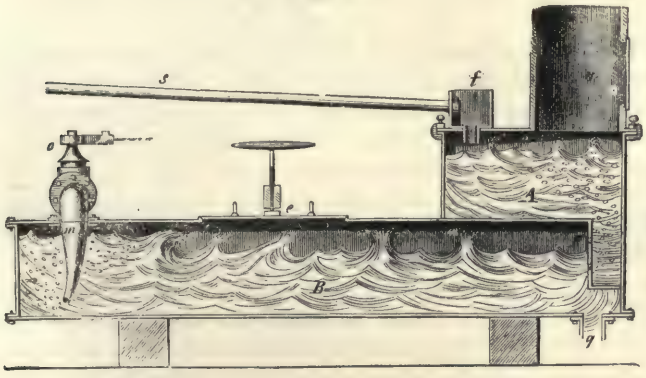
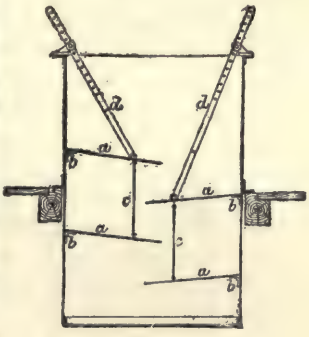


Fig. 483.



water, is admitted by the pipe, *m*, which dips nearly to the bottom of the vessel, *B*, and is divided internally by a partition for the better dissemination of the gas. The unabsorbed gas collects in *B* over the juice, whence it passes through the opening, *p*, into the upper chamber, *A*. When the juice sinks through *p* into *B*, the gas there collected passes through *A* into *n*, and is thence re-conducted to the reservoir. When the juice is sufficiently cleared, the carbonic acid cock, *o*, is turned off, and the juice allowed to flow into a reservoir through *q*, where the carbonate of lime settles. The clear juice is then fit for crystallisation. The man-hole, *e*, is provided for the cleansing of the apparatus from separated calcium carbonate. The juice to be de-limed is supplied to the cistern, *B*, by means of the pipe, *s*, and the gutter, *t*.

Other Methods of De-liming the Juice.—Instead of employing carbonic acid or animal charcoal, the lime of the sugar-lime may be removed by the addition of a substance or an acid, which forms with it an insoluble body, but does not affect the sugar.

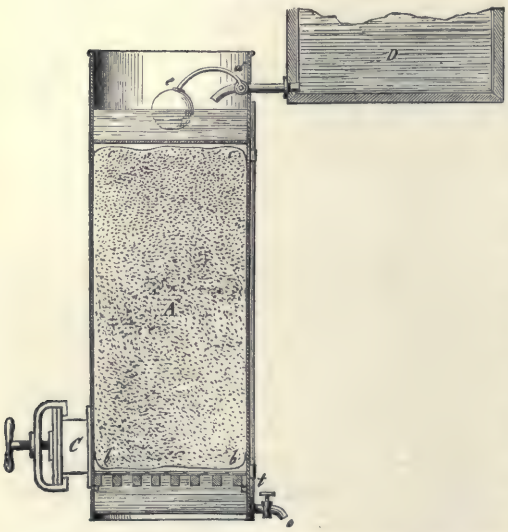
Oxalic acid is suitable for this purpose, calcium oxalate being insoluble in the sugar solution, but the acid is very expensive, and, besides, the precipitate is too fine, passing through the filter. Phosphoric acid is used for the purpose, calcium phosphate separating into flakes, which can be easily removed by filtering through a thin layer of charcoal. Any free phosphoric acid is converted into ammonium phosphate, neutralising the alkali, while the excess of ammonia is volatilised on the application of heat to the juice. Oleic, stearic, and hydrated silicic acids, and casein, similarly throw down precipitates. Acar uses pectic acid, which forms with the lime an insoluble pectate. Morgenstern has found a magnesium sulphate prepared from the Stassfurt kieserite successful in removing part of the impurities as well as a portion of the colouring matter. Frickenhaus tried hydrofluoric acid. In 1811, Proust recommended calcium sulphite; and in 1829 Dubrunfaut took out a patent for the employment of sulphurous acid. Melsens, of Brussels, in 1849, employed hyposulphurous acid, which at 100° separates the lime and most of the protein substances, and disguises for a time the colouring matter; the colour, however, returns on exposure to air, and remains permanent.

Purifying with Baryta.—About fifteen years ago, Dubrunfaut and De Massy patented a method of purifying the juice by means of caustic baryta, which forms with cane sugar at the boiling-point the insoluble saccharate, $C_{12}H_{22}O_{11}.BaO$; in practice, sufficient caustic baryta is added to throw down all the sugar. The sugar-baryta is thus separated from the supernatant fluid, in which all the foreign substances remain suspended; and is next treated with carbonic acid to form barium carbonate and set the sugar free. The solution is then filtered and some gypsum added, which gives rise to the double decomposition of the barium carbonate into sulphate, and of the gypsum into calcium carbonate.

The purification of the juices by means of electricity does not seem to have a future.

Filtration through Animal Charcoal.—The purpose of filtration is to remove a part of the non-saccharine constituents of the juice. Bone-black was first introduced into the beet-sugar manufacture by Derosne in 1812. Subsequently, Schatten observed that it removed, not merely colouring matters, but lime and salts

Fig. 484.



Dumont's Filter.—Pajot des Charmes employed animal charcoal in 1822, but Dumont was perhaps the first to make its use successful by means of a filter still bearing his name, shown in vertical section in Fig. 484 and in plan in Fig. 485. The juice is supplied to the filter, *A*, from the cistern, *D*, the supply being regulated by the ball-cock, *d e*. The pieces of charcoal in *A* rest upon the sieve, *b b*, the percolating juice being received into the cistern, and removed by the tap, *o*. *C* is a man-hole for the cleansing of the apparatus.

Instead of this filter there have been lately used sheet-iron cylinders, 5 or 6 metres in height, filled with granulated bone-black. When its purifying power is exhausted it is lixiviated with pure water, so as to recover the sugar.

To revivify spent charcoal it is covered with warm water and allowed to ferment, washed, and ignited with exclusion of air.

In Fichet's furnace the gas-fire, with the coal-shaft, *a* (Figs. 485 and 486), and

Fig. 485.

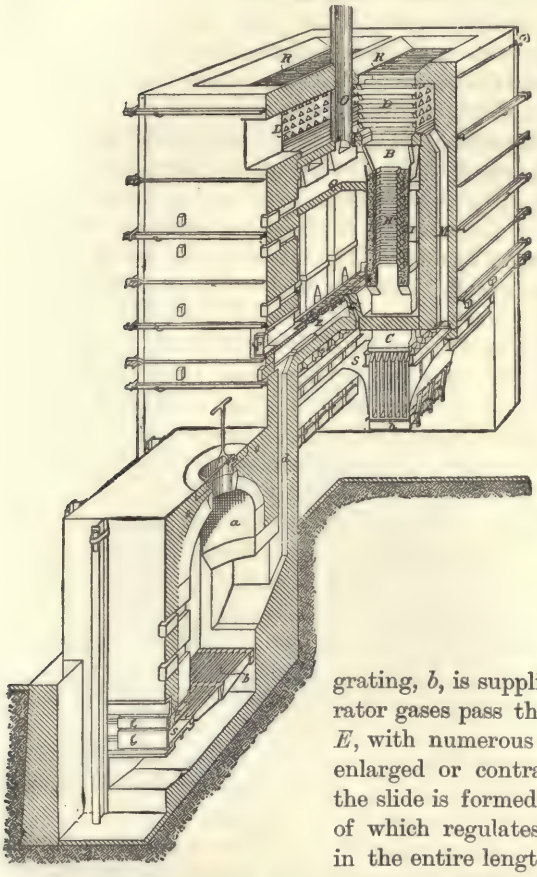
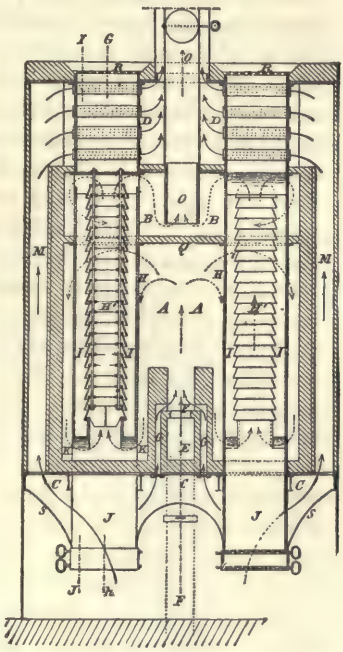


Fig. 486.



grating, *b*, is supplied with fuel from above. The generator gases pass through the channel *d* into the channel *E*, with numerous burner slits in its top, which can be enlarged or contracted by means of a common slide; the slide is formed of a plate of fire-stone, the position of which regulates the access of the combustion gases in the entire length of the channel *E*. When this has been once arranged there is nothing more to be done but to keep up the same heat. The air serving for combustion enters at *G*, but is previously warmed at the tubes, *J*, which are surrounded for this purpose with an iron screen, *S*. It effects the greatest development of heat at *F*; therefore here small especial protective walls are constructed for the lateral ignition spaces. The fire gases do not pass in a straight current to the chimney, but the draughts are so arranged that the action upon the charcoal takes place in several distinct spaces, called zones. The charcoal passes through the grating, *R*, then through the drying zone, *D*, then through the preparatory zone, *B*, then through the ignition zone, *A*, and lastly through the cooling zone, *C*. The combustion gases go upwards in the middle and give off their heat laterally to the walls or screen of the ignition-room, are then turned downwards by the cover, *Q*, and pass, as shown by the arrows, up again through *K* and *H*, and through the internal ignition spaces formed of inverted funnels placed one over the other, carry with them the ignition products issuing from the intervals of the funnels, and pass then downwards to the space *B*, where they give a preliminary warming to the charcoal intended for ultimate ignition, and escape finally by the chimney, *O*. It is easily seen that the combustion gases, on their arrival in the zone, *B*, have already given off a great part of their heat, and that the temperature in *B* will be lower than in *A*, so that the heat is well

utilised and the coal is heated by degrees. Above *B* is the drying zone, *D*, which forms the upper part of the column, and where the charcoal is kept loose by the inverted channels by which it is traversed, whilst the air which rises through *S* and *M* and is heated to 60° to 70°, passes through these hollow spaces, *D*, and dries the charcoal. This is then piled up upon the grate, *R*, in heaps of 2 metres and upwards in height, and falls slowly into the space beneath as it is drawn away below. The ignition columns are formed of funnels placed upon each other and held in their places by supports and bolts. The charcoal is now between the slanting sides of these funnels and the wall, *H*, and forms around each a free inclined plane, whilst it is heated in a thin layer from within and without, and gives off on its surface its gases to the passing fire gases. As often as charcoal is drawn away below, it falls downwards in the entire column, when the grains roll over each other, renewing the free surface and promoting the escape of gases. The cooling tubes, *J*, have ribbed or undulated surfaces, which promote the escape of heat to the air passing upwards. The hot air passes partly through *G* to the burner, partly ascends through *M*, effects the desiccation in *D*, and escapes through a pipe which surrounds the chimney, *O*, so that its heat serves to increase the draught. Suitable slides allow of a right distribution of the ascending current. The removal of the charcoal below is effected by a box, holding about 13 litres and closed by slides moved by levers. Each movement of the levers delivers 13 litres of charcoal into the truck below and fills the box for the next delivery. The workman has merely every twenty minutes to pull the levers at each column and to push away the truck which receives the carbon from three or four columns. As the heating seldom requires additional fuel, the manual labour is reduced to a very small quantity, and the correct ignition, which is regulated by the burner-register, is quite independent of the workman. The right temperature cannot be exceeded, and a delay in emptying has no bad consequences, since then the charcoal merely remains rather longer at a dull red heat, which occasions no injury. If two or three lots are withdrawn rapidly in succession it is of no consequence. If the work is partly at a stand the register in the two flues at *E* is closed to one-tenth, so that the heat in the furnace is kept up without any important consumption of fuel.

Sulphurous acid is often used for saturation, in order to be able to substitute filter-presses or gravel filters for the more expensive animal charcoal filters. Possibly animal charcoal may be ultimately dispensed with in obtaining raw sugars.

From the thin juice the water is withdrawn after filtration by two processes, known as *evaporation* and *boiling down*. The work differs according to the intended product, and is in this respect divided into three kinds—

(1) Raw sugar work;

(2) Refinery work, which is the yield of a refined product from the raw sugar;

(3) Melis work, which is a combination of (1) and (2), and aims at yielding a sugar fit for consumption directly from beet-juice.

Evaporation Pans.—The pans generally in use for evaporating the juice to crystallisation are made sufficiently strong to withstand high steam and atmospheric pressure. The processes of evaporation are—

I. Under the usual air-pressure:

- *a.* In pans suspended over an open fire;
- *b.* With high steam pressure;
- *c.* By hot air.

II. By diminished air-pressure or vacuum pans, the vacuum being produced:

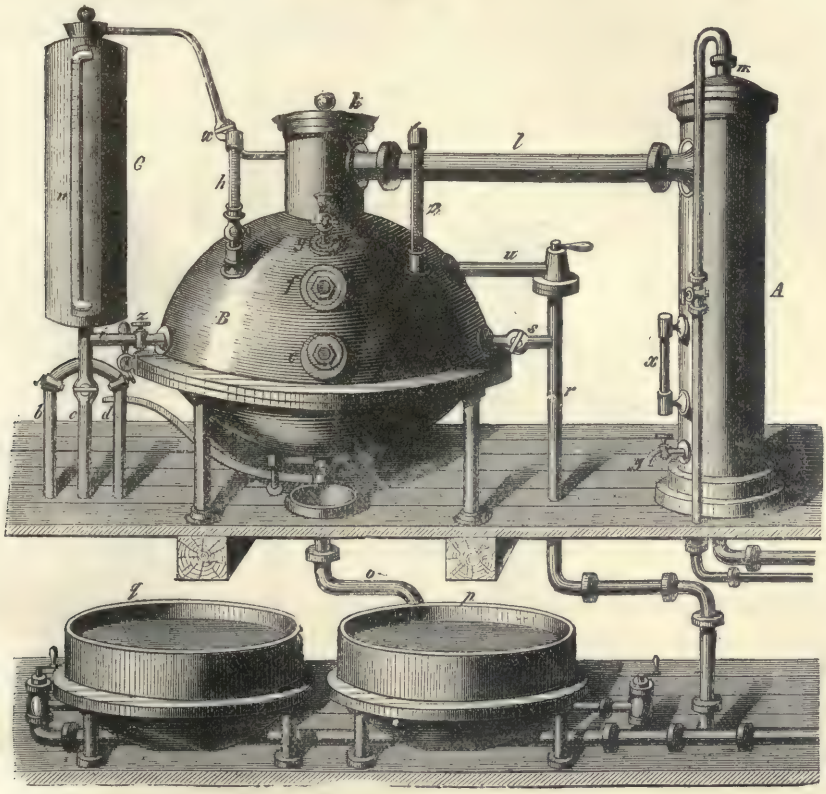
- *a.* By the air-pump;
- *b.* On the principle of the Torricelli vacuum;
- *c.* By means of steam and condensation;
- *d.* By combining the methods *a* and *b*.

The pans are constructed to prevent the boiling over of the juice. One of the bad effects of an open fire is the danger of over-heating, or burning as it is called, which deteriorates the quality of the sugar solution in various ways, forming caramel.

Evaporation in open pans has been entirely abandoned in Germany. The evaporation apparatus devised by Robert and Tischbein has introduced a new principle into the chemical arts, which comes widely into play where evaporation is necessary. The steam occasioned by evaporation in the first pan was led into a second, where it also raised the temperature. This was called the "double effect" system, or, where three vessels were used in connection, the "triple effect."

Vacuum Pans.—An improved evaporation apparatus was invented by Howard, in 1812, in which the juice was placed in chambers of rarefied air, or vacuum pans. The lowest boiling point of the clear juice in the vacuum pans is 46·1° C.; the usual

Fig. 487.

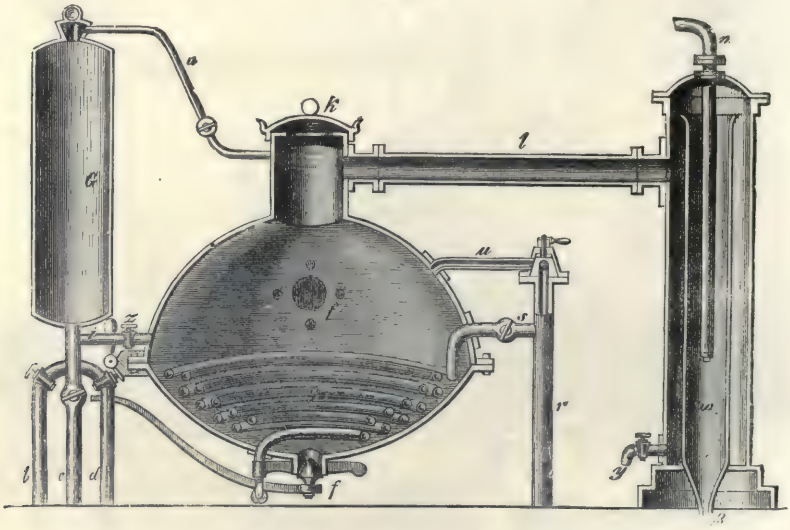


temperature at which the sugar is boiled is 65·5° to 71·1° C.; at a higher temperature the juice loses its power of crystallisation, and forms caramel. The vacuum may be considered as two distinct apparatus:—(1) The boiling pan; (2) the apparatus for exhausting the air and condensing the steam from the juice.

In France, Derosne's apparatus is extensively used; but that which we shall describe meets with general approval in Germany, and has the advantages of being simpler in construction and less costly to work. Fig. 487 is a perspective view, and Fig. 488 a section of this form of evaporating pan. The boiling pan, *B*, consists of two air-tight hemispheres, surrounded by a funnel connected by the tube, *l*, with the condenser, *A*. The apparatus is supplied with steam by *r s*, the steam circulating in the boiling pan by means of the pipes, *g* (Fig. 488). By opening the lever valves, *f*,

the juice can be run by means of the pipe, *o*, into the pan, *p*. When the pan, after continued boiling, requires to be re-filled, the pipes, *l* and *w*, are connected to an air-pump. The manometer, *h*, shows the state of the air-pressure, which can be regulated by opening the pipes connected to the vacuum chamber. By means of the gauge-cylinder, *G*, the quantity of syrup in the boiling pan can be ascertained, the gauge-cylinder being connected to the boiling pan by the pipes, *a* and *i*, and the height read off from the gauge-tube, *n*. For the purpose of ascertaining its consistency, the syrup can be removed from the gauge-cylinder by means of either of the three pipes, *b c d*. By *u* steam can be admitted to the boiling pan and condenser. *e* is generally of stout glass, through which the state of the juice can be observed. *g* is the grease-cock, butter or Sostman's paraffine being generally used to prevent the adhesion of the scum to the working parts of the pan, the taps, &c. *f* is the man-hole. The condenser consists of the jacket, *B*, arranged to prevent the mixing of the juice with the water used for condensation. *x* is the gauge. The pipe, *m*, conveying water to the condenser, terminates in a rose. *z* is a thermometer, showing the interior temperature of the boiling pan.

Fig. 488.



The air-pump being set in operation, the tube, *c*, is opened, and the gauge-cylinder filled by the juice rising from *q*. By closing *m* and opening *z*, the juice is admitted to the boiling pan. When this is half full, the steam pipe, *s*, is opened, the steam quickly heating the contents of the pan to the boiling-point. The condenser is then placed in working; by opening the pipe *l*, the steam of the juice passes into the condenser, where it is speedily condensed, passing with the water through *β*. Trappe's arrangement is sometimes found useful in working the Torricelli vacuum. The condenser is 10·6 to 11 metres above the pan; from it reaches a pipe to a water reservoir beneath, the height of the water in this pipe indicating the degree of rarefaction in the pan.

The construction of vacuum apparatus has been lately much improved.

In the apparatus of Wellner and Jelinek, with horizontal heating pipes, the bottom (Figs. 489 and 490) is formed by two sides converging obliquely. In order to open and shut the evacuation valves, *c*, at pleasure, they should be connected with the arrangement shown in the drawing. This consists of an angle-lever, *f*, turning on the bolt, f_3. With one of its arms, f_1, the valve, *c*, is connected in such a manner that

it can turn on d, whilst the second arm, f_2, leans against the lower end of a projection of the sledge, g. The sledge slides in a smaller tail-shaped groove, h, of the guiding-piece, i, and can be raised or lowered by turning the screw, j. If the screw is raised the valve opens in consequence of its weight and the pressure of the liquid, so that the contents can flow out. By screwing down g, the lever, f, is turned, and the valve is shut. The figure represents for every valve, c, a special screw, j, with its accompanying sliding-piece, g. But the arrangement can be so made that, instead of the bolt, f_2, a shaft is introduced, having as many arms, f_1, as there are valves, and which can be turned by a single arm, f_2. The heating steam circulates from the boxes, k, through the vertical tubes, l. There is also a longitudinal channel in the bottom, capable of being heated. As a sign of the sufficient concentration of the boiled juice several tests are in use. The determination of the specific gravity is not decisive. We may say in general that the boiling down may be carried from 72° to 76° Tw. (taken hot). Among the empirical tests may be mentioned the thread test. A drop of the liquid is taken up between the thumb and the forefinger, and the concentration is judged by the length to which a thread can be drawn out and the manner in which it breaks. If the juice is not sufficiently boiled the thread soon breaks. On further evaporation, it can be drawn out as far as the separation of the fingers will allow. If the thread tears about mid-length, and the upper part contracts into the shape of a hook, it is considered that the concentration is sufficient. This is the "hook test." The "blow test" consists in taking a little of the boiling liquid in a flat scum-spoon, and blowing against it, when bubbles are formed on the far side, the size and irides-

Fig. 489.

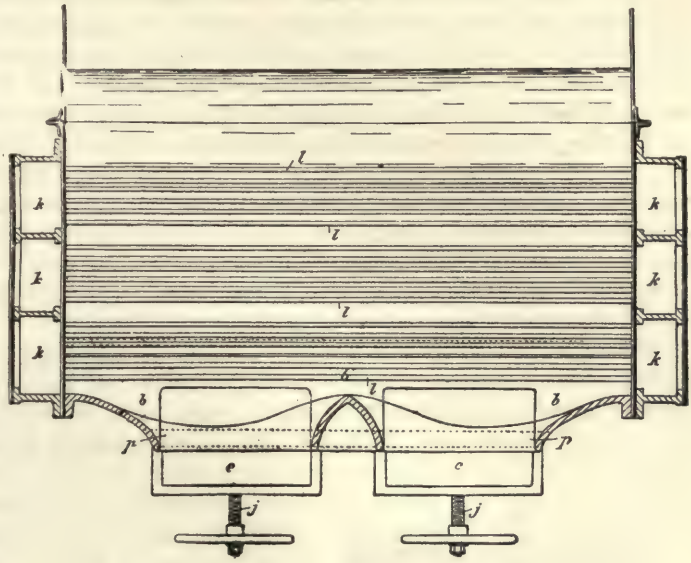
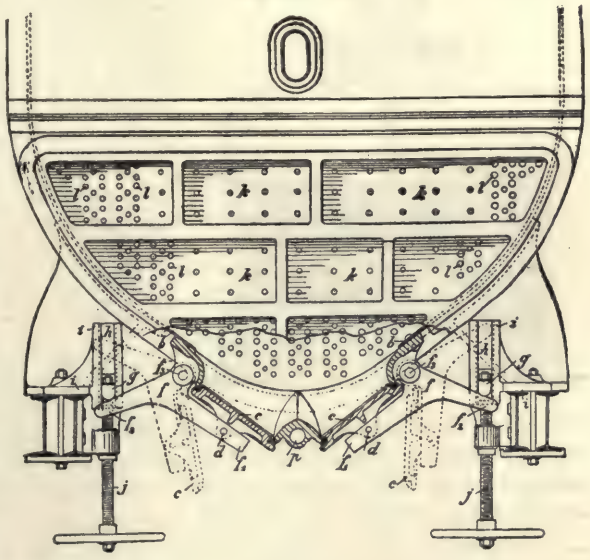


Fig. 490.



cence of which show what degree of concentration has been reached. In inferior liquids, crystallisation takes place, not in the cooler, but in the vacuum-pan.

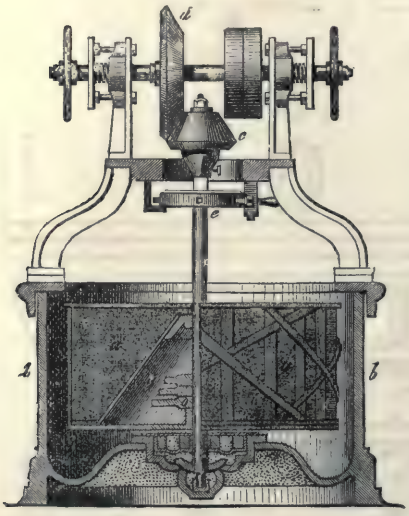
If the liquid is boiled "blank," it is a hot saturated solution of saccharose. If boiled "to crystal," it is a mixture of crystals of saccharose with the saturated solution. There are, besides, the same non-saccharose matters as in the thick juice. The water ranges from 6 to 14 per cent., and the sugar from 68 to 90. The mass may then be treated either for *raw sugar* or for *consumption sugar* (so called).

If the mass has been boiled blank, the crystallisation must be managed so as to give the largest yield of well-developed crystals. Coarse crystals can be more rapidly and thoroughly freed from treacle than the smaller crystals, and give the product a better appearance. The more concentrated the solution, and the more rapidly it has been cooled, the smaller are the crystals. In order that the crystallisation may proceed slowly, the room where the crystallisers are set (the filling-room) is heated to 30°–35°. The crystallisers hold from 1 to 20 hectolitres. Beneath the spout through which the mass passes from the vacuum to the filling-room there is a flat dish, the so-called cooler, in which it is allowed to remain until it has grown tough from the formation of crystals. It is then poured into the crystallising vessels or forms.

If the mass has been boiled "to crystal," the mass is filled direct from the vacuum into the forms at a temperature of 50°–60°.

When the crystallisation is finished, the next step is to separate the crystals (first product) from the syrup. This is generally effected in a centrifugal. The most important part of the instrument is a drum, open above (*a*, Fig. 491), of a fine metallic tissue, strengthened externally by iron bands. It is made to revolve in a cast-iron frame, *b*, at a speed of 1000 to 1500 rotations per minute. To this end the iron axle, *e*, contains at its upper end a conical friction wheel, *c*, covered with leather, and turned by another conical wheel, *d*. The inner part of the drum is contracted by a sheet-iron cone, *g*, by which the sugar to be dried is brought more to the margin of the drum, and room is obtained for three heavy pieces, which serve to maintain the equilibrium of the drum in its rapid rotation. According to the nature of the mass, from 30 to 50 kilos. are put into the centrifugal; the mass rises up on the sides, and the syrup issues through the meshes of the wire gauze, whilst dry sugar remains behind.

Fig. 491.



The syrup remaining from the coarse sugar is boiled in the vacuum pan, and worked up to a filling mass, from which a second product and a syrup from the second product are obtained. The latter, on repeated boiling, yields a third product, and the syrup of the latter again yields a fourth product, and, as a final residue, treacle. The second product is mostly sold mixed with the first. The third and fourth are thrown into the thick juice to improve its quality.

Consumption Sugar.—Raw sugar from the beet, known as consumption sugar, is distinguished from that of the cane by containing substances of a disagreeable smell and taste.*

* It must be remarked that even the most carefully refined beet sugars possess a remnant of this taste, which can be detected by experienced sugar buyers, and much more readily by bees, which reject beet sugar if cane sugar is at hand. It may be added that raw beet sugar is some-

"Consumption sugar" is met with in commerce in three forms—(1) As *crystal sugar* (something like the form in which cane sugar was produced by Finzel's process); (2) as *juice-melis* (with its modifications, cube sugar and pilé); and (3) as *farin*. The first kind consists of distinct, isolated crystals; melis is a heap of agglomerated crystals, which either takes the form of the crystallising vessels, or is broken into lumps or into fragments as pilé; farin is sugar ground to a fine meal, the crystalline appearance being intentionally destroyed.

For the production of crystal sugar the clear liquor is boiled slowly and continuously in the vacuum pans, with a reduction of temperature towards the end, so as to produce distinct crystals. The contents of the vacuum pan are washed into the centrifugal with syrup. Some of the syrup adheres to the crystals after whizzing, and has to be removed by washing the crystals, the so-called "covering."

"Covering" is resorted to in obtaining all the finer sorts of raw sugar, and is either water covering, syrup covering, steam covering, or steam-vapour covering. Water covering is effected by spirting water into the revolving drum, which dilutes and washes away the syrup, but involves a considerable loss of sugar, and has therefore been mostly given up. Washing the crystals with a clear, saturated solution of sugar is in very general use, both in the centrifugal and in the moulds. The liquid thrown out is added to the thick juice. Steam washing is effected by admitting steam at a low tension, which condenses to drops, and acts in the same manner as water. The steam-vapour covering consists in admitting into the drum a mixture of steam and air cooled down to 50°.

Melis is the commonest kind of consumption sugar, and is obtained either directly from the juice or by adding sugar to the concentrated syrup. The quality of the melis depends upon the proportion and the purity of the sugar thrown in. If much is added, and if sufficient animal charcoal is used, it cannot be sharply distinguished from refined sugar. As it retains a slight yellowish tone, it is got up with ultramarine, which masks the natural tone and gives the product a bluish-white reflection.

The forms or moulds hold from 15 to 17 kilos. of filling weight, and yield loaves of from 10 to 12 kilos. in weight. These moulds are of sheet-iron, lined with enamel. The point after filling is turned downwards, and a tube is attached, through which the syrup runs off.

Melis is sold as cube sugar and as pilé. To produce the former the mass is run into plates and converted into cakes of equal size. Pilé is a coarse melis, produced in Austria for the Italian market.

Farin is a ground consumption sugar, made up of products which would be unsaleable in their original form.

Sugar-candy.—The large, hard crystals formed during the various stages of sugar manufacture are known as sugar-candy. The commercial article is generally obtained from cane sugar, the crystals of beet-root sugar being too long and flat. The amount of sugar-candy made from beet sugar does not exceed 20 per cent. of the entire production. The sugar selected for candy is mixed with 3 to 4 per cent. of animal charcoal, then cleared with white of egg, and filtered. It is next boiled in a copper or enamelled-iron pan over an open fire, whence it is conveyed to a crystallising vessel, the sides of which are perforated with a series of holes, in eight or ten concentric rings, the distance between each hole laterally being less than that between each ring. Through these holes the candy crystallises, the size of the holes being adjusted to the consistency of the boiled sugar by means of a paste made of fine clay, ashes, and ox blood. The temperature of the drying-room is maintained at 75° for six days, when it is reduced to 45° or 50°, and in eight to ten days the crystallisation is complete. During the crystallisation the candy must not be moved or shaken, or the

times coloured with a coal-tar yellow dye, and is then exported to England for sale as "Demerara." This is done with the double purpose of obtaining an illicit profit, and of injuring the reputation of cane sugars.—[EDITOR.]

air allowed to affect it. Upon the completion of the crystallisation, the candy is found covered with a mixture of syrup and small crystals; these are removed by filling the crystallising vessels with weak lime-water. The rinsing water must be lukewarm, as cold water cracks the crystals, and hot water makes them blind, as it is technically termed. The crystallising vessel, when emptied of the rinsing water, is soaked to remove all saccharine matter, and, if this be not effected with hot water, a smooth stone is used to knock away the adhering crystals. After standing a day to dry, the sugar-candy is ready for the market. It is commercially known as of three kinds—the finest, refined white, has a large colourless crystal; yellow candy, a straw-coloured crystal; and brown candy is similar in colour to ordinary moist sugar. In some parts of France a dark candy is manufactured under the name of *Sucre de Boerhave*. Inferior cane sugar is employed for the brown, boiled sugar for the yellow, and refined sugar for the white candy. Sugar-candy is extensively used, the white principally in preparing "liqueur," a solution of candy in wine or cognac; also in the champagne manufacture, and in all cases where a clear sweetening solution is required in large quantities. The yellow candy is used for sweetening tea and coffee in restaurants, and enters largely into the recipes of the pharmaceutist for affections of the throat and chest, as well as for making syrups intended as vehicles for nauseous medicines.

Beet Treacle.—The last residual syrup contains on an average in 100 parts—

Sugar . . .	50
Non-sugar . .	30
Water . . .	20

Of the 30 parts which are not sugar, 10 parts consist of mineral matter, chiefly potassium salts (always including nitrate); the remaining 20 parts comprise oxalic acid and betain combined with inorganic bases, nitrogenous matter, derivatives and decomposition products of albumen, protoplasm, cellular tissue, &c. In consequence of the offensive taste and smell of beet treacle it is rarely admissible as an article of human consumption.

In making up this treacle, the chief processes are the osmose, the treatment with lime and spirit, or water, and the strontia process.

The osmose process depends on diffusion through parchment-paper, and is of importance, as the treacle contains a number of constituents which differ greatly in diffusive power. The saline matters diffuse very rapidly, the saccharose more slowly, and the other matters with great difficulty or not at all. But the difference in the rate of diffusion is not sufficient for a direct method of separation. At the commencement of the process large quantities of the salts pass through the parchment-paper and little saccharose. Afterwards the proportions are inverted. The osmotic process is therefore interrupted when a part of the salt has been removed, so that a part of the saccharose crystallises out on evaporation, and the treacle whizzed out from the sugar crystals has nearly the same composition as ordinary treacle. This second treacle is again freed from salts osmotically, until there finally remains a treacle so contaminated with colloid matters as not to admit of further treatment. The yellowish-brown osmotic water contains all the diffused bodies, salts, and varying quantities of sugar. It is used in irrigating meadows (for which the presence of sugar renders it questionably suitable). The process requires little initial outlay. One quire of parchment-paper serves for 540 kilos. of syrup.

Elution.—This process, devised by Scheibler in 1865, depends on the formation of a tribasic calcium saccharate and its lixiviation with alcohol at 30 per cent., in which the chief part of the non-sugar dissolves, whilst a fairly pure saccharate remains. The difficulty of obtaining a dry compound of treacle and lime was overcome by Seyferth, who takes a concentrated treacle at 80° Tw. and mixes it with freshly burnt lime in fine powder. One mol. of saccharose in the treacle requires 3 to 4 mols.

quicklime. The lime treacle, after lixiviation with alcohol, is freed from alcohol by means of steam, and then converted into a sugary milk of lime, which is pumped into large cisterns and run into separating pans. The elution-lye is worked up for alcohol. Elution yields about 80 per cent. of the saccharose present in the treacle in the state of a saccharate.

Substitution and Separation.—As elution and similar processes consume much alcohol, Steffen obtained by his process a tolerably pure calcium saccharate from water.

The treacle to be worked up daily is placed in tanks capable of containing water equal in weight to ten times the mass, and mixed with cream of lime at 54° Tw. The dilution with water is so managed that the solution gives a precipitate on heating to 100°. To the diluted treacle so much lime is added as can dissolve in the liquid—*i.e.*, about 28 parts of pure lime to 100 parts of sugar in the solution. The cisterns, each of which has a capacity of 20 cubic metres for the reception of 10 tons of treacle, are fitted with agitators. When the lime has been dissolved for eight hours, the lye is heated to 110°, in closed boilers, by means of steam, so that the insoluble sugar-lime separates out, when the entire contents of the boilers are forced through filter-presses, which are so arranged that the cakes can be lixiviated with water at 110°. The cakes are then wrapped in press-cloths of ticking, placed in a hydraulic press, and submitted to a pressure of 100–150 atmospheres. During filtration the lye must not cool down below 100°, and hence the filter-presses are heated with steam before the admission of the liquid.

The mother liquor running from the presses is allowed to cool, and a quantity of sugar, corresponding to the sugar-lime which has been precipitated again, is added in the state of a saccharated cream of lime. The mother liquor so treated is stirred for three hours at the common temperature until the liquid is saturated with lime. The mother liquor is then, by means of substitution, equal in percentages of sugar and lime to the original lye. The mother liquor is then heated in the boilers, when, on the application of heat, sugar-lime again separates out, or is filtered out and pressed. The quantity of sugar contained therein is equal to the total sugar which has been substituted. Substitution and precipitation are repeated with the same mother liquor twenty to twenty-five times, until it can be no longer treated, owing to the accumulation of salts and non-saccharine matter. The sugar-lime obtained is made up in water into a liquid of 14° Tw., and is then further treated like beet-juice.

For the separation process, the treacles, syrups, &c., are diluted with cold water in a cistern fitted with an agitator. The temperature of the solution must not exceed 35° Tw., and its concentration must correspond to 6·12 per cent. of sugar. A certain quantity of this cold solution is run into a vessel fitted with an agitator, and to every 100 parts of sugar there are added, by means of a measuring cylinder, 50–100 parts of ground lime. The whole is then pumped into the so-called lixiviation filter-presses in order to remove any excess of undissolved lime. For 100 parts of sugar in solution for medium qualities of lime, and at temperatures below 35°, 65 parts of lime are mostly sufficient to separate the sugar. When the lime has been stirred in for a short time the sugar is deposited. The paste is pumped into a second group of lixiviation filter-presses, which separate the sugar-lime from the liquid. This liquid, which contains but little sugar, and almost all the non-sugar, is either run off as a waste liquor or the same process is repeated a second time. To remove the liquid still adhering to the sugar-lime, it is purified with cold water in the filter-presses. The sugar-lime cakes are taken out of the press, ground up in a wet mill with beet-juice and solutions of sugar or water, and the sugar then separated from the lime.

Fig. 492 may serve to elucidate the entire process. Into the so-called cool-masher, *A*, which serves for forming and precipitating the sugar-lime, the treacle from

the measuring vessel is put, whilst the washing liquor of the sugar-lime presses flows in from the cistern, *C*. The lime, which has passed through a wire sieve with 2000 meshes per square centimetre, passes through the measuring vessel, *D*, generally made as a drum with four wings, so that the space between the wings contains 4 kilos. of lime dust.

Fig. 492.

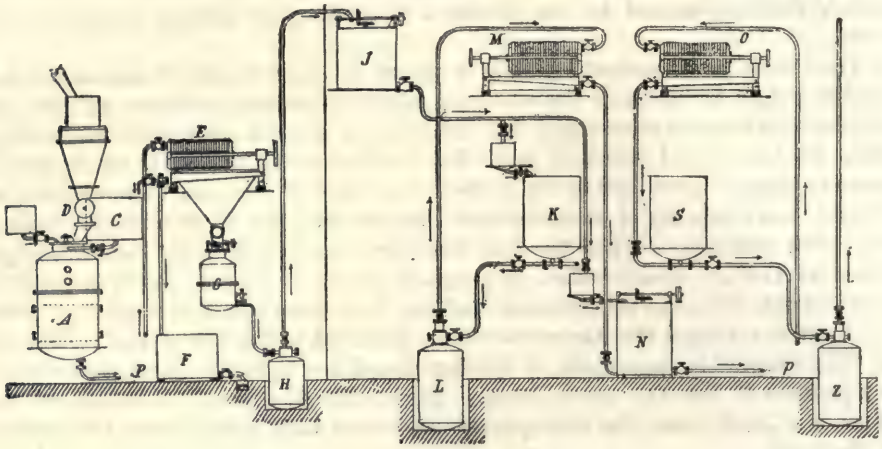


Fig. 493.

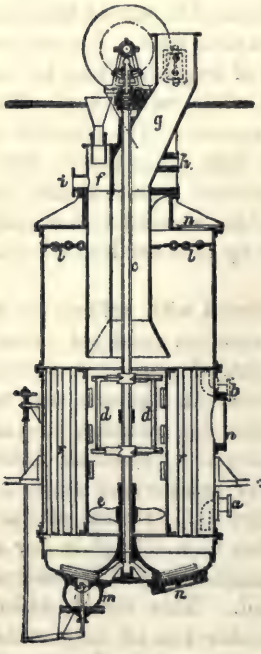
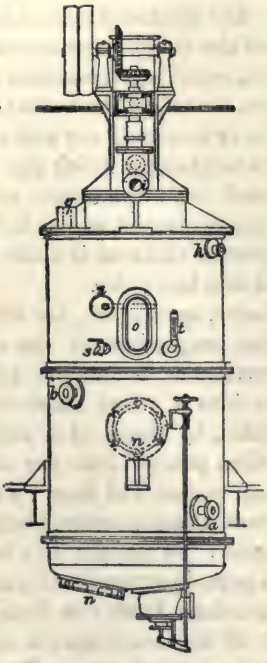


Fig. 494.



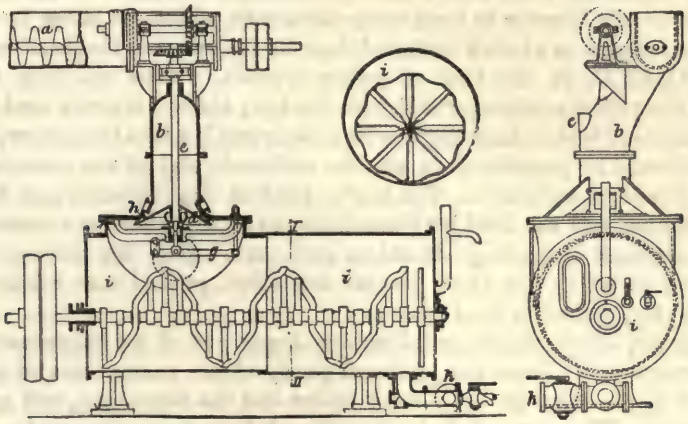
The cooling-masher shown in Figs. 493 and 494, is one-fiftieth of its real size, consists of a cylinder, with the tubes, *r*, inserted, which are surrounded by cold water in the direction from *a* towards *b*. The shaft, *c*, in the interior wide tube, carries the wings, *d*, and the mixing screw, *e*. The treacle is run in by the tube *f*, the lime by the tube *g*, the water, or the washings, by the pieces, *k*, into the worms, *l*. These are provided with fine apertures, from which the liquid passes down. The lime treacle formed is let off by the valve, *m*. The apparatus is fitted with man-holes, *n*; eye-glasses, *o*; thermometers, *t*; air-pipe, *q*; short pieces, *z*, for cleaning the eye-glasses; and a trial-cock, *s*. The treacle, as already mentioned, is diluted with water so as to form 25 hectolitres of liquor, containing about 7 per cent. of sugar. It is then cooled as far as possible by letting in the cooling water and putting the agitating screw, *e*, in action. The lime-dust is then gradually added. The cooling water, six times the weight of the treacle, enters at 8° and escapes at 12°. The entire contents of the cooling-masher are forced through the filter-presses, *E*, by a pump at *P*. From these there first flows off a lye which contains scarcely any sugar (polarising only 0·5 to 0·6), and is, therefore, at once

allowed to flow off. As the saccharate has a granular crystalline texture, it can be washed in the same presses with cold water, in which it is almost insoluble.

The washings are also allowed to flow away, but that finally obtained is used to dilute the treacle, and it is for the present collected in the cisterns, *F*. The saccharate from the filter-presses is a white, sandy mass, and it is converted in the sugar-lime mill, *G*, into sugary milk of lime, and forced by the montejus, *H*, into the cistern, *J*, where it stands ready for further use.

The sugar-lime mill is shown in Figs. 495, 496, and 497 at one-fiftieth of its actual size. The spiral, *a*, which lies below the filter presses, moves the sugar-lime into the body, *b*, which lies above the guiding piece. If a diluting liquid is used, it enters at *c*. The guiding-piece is constructed after the manner of coffee-mills. A conical toothed

Fig. 495. Fig. 496. Fig 497.



disc, *d*, is fixed on a vertical shaft, *e*, the track of which can be raised by the lever, *g*, so that the teeth of the disc, *d*, can be set exactly opposite those of the edge, *h*. The ground product falls into the horizontal mash-drum, *i*; is here well worked through, and is drawn off at *k* as ready milk of lime. If only so much treacle is worked up that the lime in the saccharine milk of lime can be entirely used for separation in the sugar vats, the saccharate is immediately mixed with beet-juice in the mill. But if the lime would be too much, a part of it has first to be removed. It is mashed, therefore, in the mill with the thin juice, or with the juice of the first saturation. The excess of lime, two-thirds of that originally combined with the sugar, is separated out in filter-presses, and the solution, which now contains 25 to 30 of lime to 100 of sugar, is then passed on to saturation.

The Strontia Process.—Dubrunfaut proposed, as far back as 1849, to separate sugar out of treacle by means of strontia or baryta, and in 1863 Stammer showed that, on working up treacle by means of strontia, a much purer product was obtained than with lime. He considered the process as impracticable on account of the difficulty of procuring strontia. Meantime the Dessau sugar refinery used strontianite with success, though the details of the process were unknown. The process has recently been developed by Scheibler.

The treacle is intimately mixed with a hot saturated solution of strontia; the mixture passes through a cooling apparatus and arrives at the crystallisers, where, after the addition, if necessary, of a little strontium non-saccharate to induce crystallisation, it congeals completely to mono-strontium sugar, $C_{12}H_{22}O_{11}SrO.5H_2O$. The congealed mass is then again liquefied by agitation and passed through the filter-presses, when it is resolved into *A*, non-strontium sugar, and *B*, sacchariferous lye.

The worked, white saccharate cakes, *A*, from the filter-presses are mashed up with

water or beet-juice, and saturated with water only so far that there remains an alkalinity of 0·04 or 0·06 SrO. The precipitated strontium carbonate is then separated from the solution of sugar by filter-presses; the white mud of $SrCO_3$ is made up into bricks for the oven, whilst the filtered sugar-juice undergoes a second saturation in order to be entirely freed from SrO. It is boiled up and filtered again in order to separate the white $SrCO_3$ mud from the pure solution of sugar. The press mud goes to the brick-pressing machine, whilst the thin juice obtained is worked up after filtration to filling mass in the ordinary manner, or prior to filtration it is mixed with separated and saturated thin juice, in order to be worked up together.

The above-mentioned saccharine-lye, *B*, is mixed up with the required quantity of caustic strontia, and boiled; the sugar is separated out as bi-strontium sugar in the form of a dense precipitate, which rapidly subsides. The precipitate and the lye are most easily separated from each other by settling; the former serves at once for mixing with treacle in order to form mono-saccharate, whilst the latter is passed into special large cisterns, in which it cools and deposits the excess of the dissolved strontium salt, $Sr(OH)_2.8H_2O$, in the form of yellow crystals. After standing for two or three days, the yellow salt is separated from the lye; the salt is again used for forming mono-saccharate or bi-strontium sugar, whilst the brown lye, free from sugar, is saturated with carbonic acid in presence of an alkaline carbonate, and all the strontia is thrown down as a strontium carbonate. The brown product thus obtained goes to the brick-pressing machine, and the final lye (containing no sugar) is used as a manure. Caustic strontia is obtained by igniting strontium carbonate. Both the commercial strontia and that recovered by the above process are dried, pressed into bricks, and, after thorough drying, ignited in the furnace.

Palm Sugar, Maple Sugar, and Sorghum Sugar are of no importance so far as Europe is concerned. There are produced yearly about 12,000 tons of palm sugar, 2500 tons of maple sugar (in the United States and the Dominion), and 3000 tons of Sorghum sugar. The cane and the beet yield each from two to two and a half million tons.

FERMENTATION ARTS.

Fermentation and Yeast.—Fermentation is a term applied to the peculiar changes of complex organic substances of the amylaceous and saccharine type under the influence of certain putrescible nitrogenous substances or ferments. The decomposition of fermentable organic bodies by a ferment effects the separation of their constituents into two or more combinations, as when by a yeast-ferment dextrose and levulose are converted into alcohol, its homologues, and carbonic and succinic acids; or the molecules of the original substance are re-grouped, as in the conversion of sugar of milk into lactic acid during lactic-acid fermentation; finally, the elements of the organic substance may enter into combination with the oxygen of the atmosphere either to form new organic combinations, or to separate into its inorganic constituents carbonic acid, carburetted hydrogen, &c. This latter decomposition is termed *mouldering* when a residue rich in carbon (humus) remains, but when only the mineral constituents remain, *decay* is said to have been reached. These terms are thus defined more by custom or usage than by direct etymology—dictionaries hardly distinguish between them, but the difference is known to all. If large quantities of water be present both these processes are resolved into *putrefaction*, in which chiefly gases—carbonic acid, ammonia, sulphuretted hydrogen—and water are disengaged. But fermentation always results in the remaining or the formation of other organic compounds, and the variety of fermentation set up mostly depends on the state of decomposition of the azotised matter employed as a ferment. The most important ferment is undoubtedly yeast, but the ferment may be either an organic substance (yeast) or a protein body in

a putrescent state—it is always a nitrogenised body. In a technological work the varieties of fermentation may be classed as—

1. Vinous or alcoholic fermentation, including the changes observed during the processes of wine making, beer brewing, and the production of alcoholic liquors or spirits.
2. Lactic-acid fermentation, taking place during the souring of milk; and at a higher temperature changing to
3. Butyric-acid fermentation.

To these fermentations may be added—

4. Putrescence, noticeable only in technological chemistry as a stage to be most carefully avoided.

Vinous Fermentation.—Vinous or alcoholic fermentation is the result of the decomposition of saccharine matter, dextrose or glucose, levulose or chylariose, and lactose into several products, principally alcohol and carbonic acid. According to the recent researches of Lermer and Von Liebig (1870), dextrine in the presence of sugar is converted into equal parts of alcohol and carbonic acid.

Dextrose, according to the equation $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, yields 51·1 per cent. alcohol and 48·9 carbonic acid, saccharine, and maltose—

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2.$$

In the latter process 132,000 heat-units are liberated, or 720 per kilo. of alcohol.

Recently Pasteur has shown that lactic acid does not result from alcoholic fermentation, but that succinic acid is a constant product of this fermentation in quantities never less than 0·6 to 0·7 per cent. of the weight of the sugar employed. Glycerine is another constant production to the extent of 3 per cent. of the sugar; this substance occurs in all wines. The 5 to 6 per cent. of substances remaining may therefore be thus divided:—

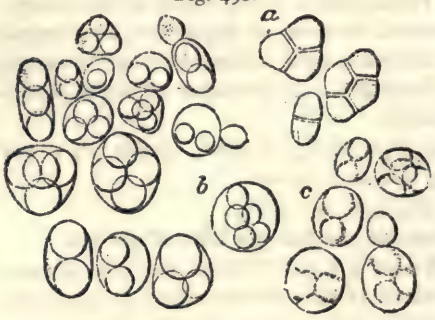
Succinic acid	0·6 to 0·7
Glycerine	3·2 to 3·6
Carbonic acid	0·6 to 0·7
Cellulose, fatty substances, &c.	1·2 to 1·5
	5·6 to 6·5

Yeast.—The nature of alcoholic fermentation was first investigated by Cagniard-Latour, while our present knowledge is due chiefly to the researches of A. de Bary, J. Wiesner, Hoffman, Bail, Berkley, Pasteur, Hallier, Béchamp, and Lermer. Yeast on being introduced into a fermentable fluid rapidly throws out fermenting arms, as it were, until the fluid is covered with a *superficial* ferment, termed in German the *Oberhefe*, while at the bottom of the vessel a viscid sediment is deposited, known in German as the *Unterhefe*. The oberhefe, or superficial ferment, is employed as *barm* by the baker, for the purpose of leavening his bread; while the unterhefe, or sedimentary ferment, is that employed in the fermentation of wines and of Bavarian beers; these beers differ from the general beers of England, France, and Germany in not souring by exposure to air, this quality being due to the peculiarity in the process of fermentation, *Untergaehrung*, or fermenting from below, during which the gluten, the substance absorbing the oxygen of the air, is removed. In the distillation of brandy, the yeast employed is a mixture of *barm* and *bottom* yeast, as the terms run in this country. Fresh yeast appears as a grey-yellow or red froth of strong odour, and with an acid reaction. Under the microscope the two kinds of yeast are easily distinguished. The superficial yeast or barm consists of globular or ellipsoidal cells of equal size, and about 0·01 millimetre diameter. They float in the fluid partly alone, partly in groups. The walls of the cells are so transparent that the inner cells can be seen through the upper. In the centre of each cell appears a dark speck or grain, the *protoplasma*,

sometimes consisting of more than 1 grain. The bottom yeast, or sedimentary ferment, also consists of cells, but these do not cling together so tenaciously as the cells of the barm, and are generally isolated, while the adhesion is merely mechanical between those that do cling together, a slight concussion being sufficient to effect their separation. Sometimes a large cell of the bottom yeast contains two, three, or even four smaller cells, the dimensions of these cells varying greatly, and not being nearly so constant as in the cells of the barm.

E. C. Hansen distinguishes six kinds of yeast; the more important are *Saccharomyces cerevisiæ I.*, the ordinary beer ferment. It is a powerful form of a top yeast. The cells (Fig. 498) are greyish, both by reflected and by transmitted light, and more or less globular. The size of the cells varies from $2\frac{1}{2}$ to 6 micromillimetres. There are generally found in each mother cell one to four, or very exceptionally, five cells (498, *b*). The cell walls of the spaces are generally more distinct than in the other kinds. Fig. 498, *c*, shows cells with undeveloped askospores. Fig. 498, *a*, is a peculiar form of development which often occurs. The cells are divided by partition walls into several parts, each of which can send out growths.

Fig. 498.



Saccharomyces pastorianus I. is a yeast which Hansen has often collected in the air of a brewery at Copenhagen. If cultivated in wort it occasions bottom fermentation. The askospores (Fig. 499) have in general the diameter of 1·5 to 3·5 micromillimetres. There are commonly one to four askospores in each cell, but sometimes as many as ten (Fig. 499, *b*).

Saccharomyces ellipsoideus I. (Fig. 500) was collected in the Vosges on ripe grapes. It is the ordinary ferment of wines.

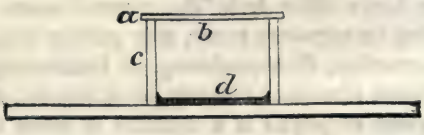
Fig. 499.



Fig. 500.



Fig. 501.



An important step in the fermentation industries is the obtaining and utilisation of pure cultures by Hansen.

The moist chamber used is shown in section on a reduced scale, Fig. 501. The cultivation is carried on on the lower side, *b*, of the covering glass, *a*; *c* is the side of the chamber and *d* is a stratum of water at the bottom to prevent desiccation. All these objects must be passed through a gas or spirit flame, or, preferably, wrapped in several

folds of filter-paper and sterilised by two hours' exposure to the temperature of 150° in an oven. The upper edge of the sides must be covered with vaseline. A water bath heated to 30°–35° is kept ready; also a stand upon which is set a Chamberland flask (Fig. 502). Two such flasks are required, each holding about 30 c.c., half full of nutrient gelatine. Their outer surfaces are passed through the flame, and they are then set under a bell till they are wanted for use. They are fitted with ground-glass caps drawn out to a slender tube, which is filled with sterilised cotton. A 5 per cent. solution of gelatine in clear hopped wort is taken as nutrient solution.

Fig. 502.



For the propagation of pure cultures, the flasks which contain the nutrient gelatine are cautiously heated until their contents are liquid, when they are placed in the water-bath. For pure cultivations young cells are taken in vigorous vegetation. A small number of them are diluted in the flask with sterilised water until it becomes slightly dull; the flask is shaken in order that the cells may be uniformly distributed; a few drops are taken out with a glass rod and examined under the microscope. A low power is used, so as to just distinguish the cells from other small accompanying bodies. The purpose of this first microscopic examination is to estimate the quantity of cells in the mixture. After it has been well shaken up, an ignited platinum wire is dipped into the liquid and quickly inserted into one of the flasks containing nutrient gelatine. The temperature of the gelatine must not exceed 35°; it is sufficient, if kept liquid, and the microscopic examination shows that the mixture is rich in cells, for the platinum wire to be plunged in only to the depth of 2 millimetres; in the opposite case it is plunged in more deeply.

For greater safety two preparations are made; if both give the same result, it may be assumed that the cells are uniformly distributed, and that average specimens have been obtained. It must next be determined whether the gelatine has received a sufficient number of cells or not. If a considerable error is committed in this respect all further work is in vain. In order that the cells may be so distributed in the gelatine that pure colonies may be obtained with certainty, the colonies which are afterwards formed must have room enough not to intermingle with each other. Such drops, in shape and size as are to be afterwards used, are placed upon an ordinary glass slip, or, preferably, on a slip where a number of squares have been marked with a diamond. The squares give a guide for the microscopic examination. If it appears that too few or too many cells have been sown, more cells must be added in the first case, and in the latter more gelatine, all being calculated beforehand. If we find that the mixture contains twice as many cells as was intended, the right point is reached by adding as much more gelatine as is already present. A corresponding portion must be at once placed upon the glass covers, which are immediately covered with a little glass bell. As a matter of course, the gelatines must be kept liquid in the water bath; the cells must be distributed by shaking, avoiding the formation of foam. At the ordinary temperature of a room the gelatines coagulate in a quarter of an hour. As soon as the gelatine is coagulated, the covering glass is fixed to the ring in such a manner that the cultivation is downwards. By a cautious pressure on those points of the glass which touch the ring the chamber is quite shut off from the outer air. When the chambers are in order they are examined with a low power. It must be ascertained whether the spots of vegetation are pure—*i.e.*, whether each proceeds from a single cell. The operations up to this point engage an investigator of some experience for three hours. The moist chambers are then placed in a thermostat at 24°–25°. If there is a microscope in reserve, a chamber may be secured to its stage in such a manner that the cell in question can be accurately seen and its development followed step by step. Spots of vegetation, visible

to the naked eye, develop in two or three days. In the *Saccharomycetes* the vegetative spots have the appearance of minute pin-heads and a pale yellowish-grey colour; the surface may be either dull or slightly shining: the margin, under a low power, appears sharply bounded or uneven. The colonies of *Mycoderma vini* and *M. cerivisiæ* and some kindred species are of a pale grey, with a dead surface, spread out like a film and hollowed like a capsule. As long as they are covered with gelatine they resemble the spots of the *Saccharomycetes*. In the gelatine film of a single covering glass sixty spots of vegetation may be developed. When the pure cultivations are transferred to the nutritive liquid the air must be pure and calm, and the apparatus must be thoroughly sterilised. A pair of small forceps and platinum wires, which have been passed through the flame, must be at hand, and a sufficient number of small bells with their glass plates. For culture in a nutrient liquid, Pasteur's two-necked flask is generally used ($\frac{1}{8}$ litre, Fig. 503) and hopped sterilised wort. The thin tube is closed at its end with an asbestos plug; to the straight tube is attached a piece of flexible tubing closed with a glass stopper. If a pure culture of a single species is desired, four or five of such flasks are needed. This number is to enable the observer to compare the vegetations developed in the flasks and ascertain whether he has obtained a growth of the cells which have been sown. It may accidentally occur that one of the flasks has been infected by a foreign organism, or no vegetation at all may be developed—*e.g.*, if the platinum wire was too hot. The chambers are examined with the microscope; the vegetations, the origin of which has been ascertained, are scrutinised so that we may be sure that the colonies arise each from a single cell. The boundaries of the selected colonies are marked out with a fine brush and a little white colour. A covering glass is then lifted off its ring, and turned upside down, so that the spots are upwards and placed, if possible, on a dark background, that they may be seen more distinctly. By means of a forceps we lift up a platinum thread, and, after drawing it rapidly through a gas or spirit flame, the selected spots are touched with it. If several specimens are to be taken from the covering glass, it must of course be covered each time with a small bell. The operator, with his left hand, removes the flexible tube of the Pasteur flask, and brings at the same moment, with the other hand, the infected platinum wire to the opening of the tube, into which it is let fall. The tube is now inclined so far that the liquid does not run out, and at the same time it is passed through the fire and again covered with the caoutchouc tube. The flasks are placed in a heat of 25°–28°. In the course of one or two days there is a well-marked development. If every foreign infection has been avoided on transferring the cells to the flasks, each flask contains a pure cultivation. A specimen is taken from each with due precautions and examined with the microscope.

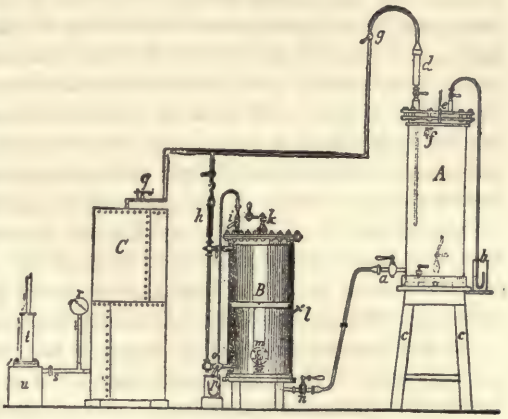
Fig. 503.



In order to obtain larger quantities of pure yeast, the receiver, *C* (Fig. 504), fitted with a safety valve, *q*, and a pressure gauge, *r*, is filled with air to a pressure of 3 to 4 atmospheres by means of the air-pump, *t u*, and the pipe *s*. The wort cylinder, *A*, provided with a trial cock, *f*, is sterilised with steam under pressure, when the air escapes through the tube, *b*, and air is admitted in its place through the cock *g*, and the cotton filter, *d*. The wort is conveyed in a boiling condition into the cylinder from the main pipe of the boiling-house. Cooling is effected by water trickling out of the ring, *e*; the air needed for aëration is let pass through the filter *d*. The fermentation cylinder, *B*, is sterilised in the same manner as the wort cylinder. It has a similar

filter, *h*; a glass tube, *o*, in order to observe the level of the liquid; a tube, *i h*, for the escape of carbonic acid; an agitator, *k*, in order to mix the yeast with the liquid; a small tube, *l*, for introducing pure yeast and for taking small samples.

Fig. 504.



The yeast is added only once, and the apparatus then works for a year, or longer if required. The outflow cock, *m*, is so arranged that the liquid itself effects the purification, and no infection from without can take place, but high tension must always be kept up. The wort is passed into the fermentation cylinder through the piping, *a n*, which connects both cylinders. As soon as it comes near the yeast tube, *l*, the pipe is closed until the yeast is added; it is then filled up to the mark in the upper part of the glass tube; it is stirred, and 220 litres of sterilised wort are thus brought into fermentation with absolutely pure yeast. In about ten days the beer is drawn off through the cock *m*. During tapping, air is let enter through the filter *h*. As soon as any mud appears the running is stopped, wort is added, stirred up, and 27 litres are taken out of this mixture of wort and yeast. Wort is added afresh, stirred again, and 27 litres are taken of this last mixture. The measures are shown by a graduation on the glass tube, *o*. In the 54 litres taken out there is yeast enough to set 8 hectolitres of wort in fermentation; the yeast remaining in the cylinder is enough to bring again 220 litres into fermentation, and so it goes on continuously.

Nägeli and Löw (1878) found in the bottom yeast of beer (with nearly 8 per cent. of nitrogen)—

Cellulose and vegetable mucus	37 per cent.
Proteines : *a*. Common albumen	36 ,,
b. Gluten casein albumen	9 ,,
Peptones (precipitable by basic lead acetate)	2 ,,
Fat	5 ,,
Ash	7 ,,
Extractive matter, &c.	4 ,,

Top yeast contains 2·5 per cent. and bottom yeast up to 7 per cent. of ash. The proportion of sulphur averages 0·5 to 0·8 per cent. The ash of the yeast consists chiefly of potassa, phosphoric acid, silica, and magnesia.

Physiologists are not agreed as to the part played by yeast in alcoholic fermentation. If the yeast is to act upon another substance, there must be interpenetration. As the yeast is enclosed in a cell-membrane, the substances upon which the yeast is to act must penetrate this membrane, *i.e.*, must be capable of diffusion. Hence malt is required in the mashing process in order to split up the starch into maltose and dextrine, the former of which is able to penetrate through the cellular membranes of the yeast. It is not sufficient for a complete conversion of the maltose into alcohol to carry out the process of saccharification, namely, at a suitable temperature. For a good fermentation, such as is required in the distilling business, the subsequent action of diastase is needed, whereby the dextrine, which is not diffusible, is gradually converted into maltose, and penetrates into the yeast cell. The thinner the membrane the better the diffusion. Old yeast is harder to nourish than young yeast, as in the former the membrane is thicker. The albuminoids are converted by the action of the peptase of

the malt into soluble and diffusible peptones, and in this state they pass into the yeast cell. There they become insoluble and are reconverted into albumens. The case is similar with the maltose, which is formed from the starch in the mashing process. A small part of it is precipitated as cellulose within the yeast cells; but in great part it is split up into alcohol and carbon dioxide, which do not form constituents of the starch. A vigorous, healthy yeast prolongs its life even if it receives no fresh nutriment. This vegetation of the yeast without nutrition is called the self-fermentation of the yeast. We have, therefore, to distinguish two stages in the development of yeast—*i.e.*, (1) the reception of nutriment and their use in the production of new cells; (2) the katagenesis, in which the substance of the yeast cell is decomposed.

Conditions of Alcoholic or Vinous Fermentation.—The conditions of alcoholic fermentation are the general conditions of the vegetation of the yeast plant, with the distinction that by vinous fermentation the largest amount of alcohol is obtained. The following conditions must be fulfilled when alcoholic fermentation is the desideratum :—

1. *An Aqueous Solution of Sugar*, in the proportion of 1 part of sugar to 4 to 10 parts of water. The sugar can be employed as grape sugar, dextrose, or levulose, which is always capable of fermentation; or an unfermentable sugar, cane sugar, or sugar of milk, may be converted by means of an acid or suitable agent into fermentable sugar. However gradual the process may seem, cane sugar is always converted into grape sugar before fermentation sets in.

2. *The Presence of Yeast or Spawn.*—In the first case, 1 part of yeast to 5 parts of sugar is sufficient to effect a strong fermentation. If spawn only is present, there must also be present substances upon which the spawn may feed or develop—protein substances, phosphoric acid, humus, and alkalies. If no ferment exists, the only other condition under which fermentation is effected is by exposure to—

3. *The Atmosphere*, which introduces the before-mentioned ferment and furnishes life.

4. *A known Temperature*, the limits of which are 5° and 30° C. As a rule, vinous fermentation is effected between 9° and 25°. The lower the temperature the longer the time required for the fermentation to subside, and conversely. At 30°, and at higher temperatures, the vinous fermentation easily goes over into butyric-acid fermentation. The making of wines is based on a practical acquaintance with alcoholic fermentation; but in this case only a portion of the sugar of the must goes over into alcohol and carbonic acid. The alcohol remains, while the greater part of the carbonic acid escapes.

Yeast, like all plants, requires for its development and increase the co-operation of atmospheric oxygen; in the absence of free oxygen yeast cannot grow in a nutritive solution. The assertion of Pasteur, that yeast can obtain the oxygen needed for its increase from oxygenous compounds (*e.g.*, from sugar), is disputed. Under suitable conditions yeast grows without setting up fermentation, and, on the other hand, it is established that fermentation occurs without the growth of yeast. The growth of yeast and fermentation are, therefore, not inseparable. The production of the "seed yeast" must ensue with abundant access of air, but the process of fermentation goes on with the completest possible exclusion of air.

Pressed Yeast (*Dry Yeast*).—Yeast may be made in various ways. At Schiedam (Holland) it is made of excellent quality by a mode which is to a certain extent a trade secret, and differs materially from the following process :—A mash is made in the ordinary manner of 1 part of bruised barley malt with 3 parts of bruised rye, the mash being cooled with the fluid portion of the wash. To 100 kilos. of the bruised grain is added 0·5 kilo. of sodium carbonate and 0·35 kilo. of sulphuric acid diluted with water; these ingredients having been added to the mash, it is brought to fermentation by the aid of yeast. The newly formed yeast is removed from the strongly fermenting fluid by the aid of perforated ladles; it is then strained through a linen cloth or fine sieve, and poured into cold water, wherein it is allowed to form a sediment.

The sediment thus produced is collected after the supernatant water has been run off, is placed in a stout canvas bag under a press, and formed into a stiff clayey dough, to which usually 4 to 10 (sometimes as much as 24) per cent. of dry potato starch is added. Sometimes the water is removed from the yeast by placing that substance upon slabs made of gypsum or other absorbent materials, care being taken to keep the yeast in a cool place; by the use of the hydro-extractor—expressly arranged as regards its construction for this purpose—yeast may be very rapidly rendered dry. As regards the use of the sodium carbonate, it appears to assist in the separation of the glutinous constituents of the cereals; the action of the sulphuric acid is partly similar, and it also prevents the formation of lactic acid, which, if formed, causes a loss of both starch and spirit; the sulphuric acid also accelerates the separation of the yeast. According to communications by some of the most eminent distillers at Schiedam to Dr. G. J. Mulder, neither soda nor sulphuric acid is used at Schiedam in the preparation of what the trade terms dry or German yeast, some of which is imported into this country from Hamburg. Assuming the researches of Pasteur and others on fermentation to be correct, these observations are of great value in reference to the manufacture of yeast. It is found that the yeast sporulæ become properly developed when they are placed in a fluid which, instead of containing protein compounds, consists of aqueous saline solutions mixed with a sugar solution, such as, for instance, ammonium tartrate, potassium and magnesium phosphate, and gypsum. It would hence appear that under such conditions yeast cells take up the material for the propagation of new cells, partly from inorganic substances, partly from organic, viz., the decomposing sugar which yields carbonic acid: in this respect the yeast cells agree, then, with higher organised plants. As regards the quantity of yeast obtainable from a given weight of materials, it may be stated that from 100 kilos. of rye, including the bruised malt, about 15 to 16 kilos. of dry yeast can be obtained. As the quantity of real yeast or of the nitrogenous matter for sale present in the ready prepared dry yeast amounts at the most to 20 per cent., the nutritive value of the wash obtained after the distilling off of the spirits from the fermented liquid is but little impaired.

In testing yeast a portion is placed in solution of sugar, and the carbon dioxide formed is determined gravimetrically or volumetrically.

The industries based on alcoholic fermentation are—

1. The production of wine. The alcohol is not separated from the fermented liquid. If the fermentation is suppressed, a portion of the carbon dioxide formed remains in solution and escapes with effervescence on the removal of the pressure (champagnes).

2. Brewing, in which the substance forming alcohol is chiefly starch. A part of it is changed into non-fermentible dextrine, but the greater part into maltose, which is decomposed on fermentation. A small part of the sugar serves to keep up a secondary fermentation, which is retarded as much as possible by a reduction of temperature, whilst the gradual escape of carbon dioxide contributes to the preservation of the beer. Here also, as in the case of wine, the alcohol is not separated from the fermented liquid.

3. Whilst, in brewing, a part only of the starch used as a raw material is converted into maltose, and is only by degrees transformed into alcohol and carbon dioxide, the object in a distillery is to obtain from the given material (starch or sugar) in a minimum of time a maximum of alcohol, which is separated from the fermented liquid by distillation. The secondary fermentation is conducted so that the yeast destroys itself.

WINE MAKING.

By the name of wine is generally distinguished an alcoholic fluid prepared without distillation by the fermentation of grape-juice. In the widest meaning of the term is included the result of the vinous fermentation of all natural juices.

The Vine and its Cultivation.—The vine, *Vitis vinifera*, is generally cultivated in Europe at a temperature of 50°, while the best and ripest drinking wines are obtained from grapes grown at a temperature of 51° to 52°. It requires an average temperature of 10° to 11°, and an average summer temperature of 18° to 20°; but it is the summer's sun that forms the sugar. A climate with severe winters and hot summers is therefore as favourable to the cultivation of the grape as a temperate climate. England, with a mean average annual temperature of 11°, is consequently very unsuited to the growth of the vine. The weather has the greatest influence upon the vine: during the growth rain is required, but during the ripening only the sun's rays should reach the grape. The soil is not so much a matter of consequence if a quantity of potash be present; but a warm, loose soil is the best.

Volcanic soils, rich in potash, such as those of the banks of the Rhine, of the Greek islands, and of Southern Italy, are most suitable for the vine. The wines produced at high latitudes on the continent of Europe, *e.g.*, at Grünberg, in Silesia, are of a very low character.

Besides serving for the production of wine, grapes are used for immediate consumption, and also dried in the state of raisins. They are also employed in the preparation of (genuine) grape sugar, and in the manufacture of cognac, wine-vinegar, &c. An oil is obtained from the seeds, and the lyes are the principal raw material for the manufacture of tartar and tartaric acid.

Vintage.—The sugar is found at an early stage of the growth of the grape. When unripe the grape contains malic, citric, and tartaric acids, potassium and calcium bitartrate, organic salts in smaller proportions, and a little colouring and extractive matter. Successive analyses have been made of the grape during its period of growth by C. Neubauer from samples obtained from the Neroberg, near Wiesbaden (1868), and have given the following results:—

July	27th	.	.	0·6	per cent.	sugar and	2·7	per cent. free acid
August	9th	.	.	0·9	,,	,,	2·9	,, ,,
,,	17th	.	.	2·3	,,	,,	2·8	,, ,,
,,	28th	.	.	8·2	,,	,,	1·9	,, ,,
September	7th	.	.	11·9	,,	,,	1·2	,, ,,
,,	17th	.	.	18·4	,,	,,	0·95	,, ,,
,,	28th	.	.	17·5	,,	,,	0·8	,, ,,
October	5th	.	.	16·9	,,	,,	0·8	,, ,,
,,	12th	.	.	18·6	,,	,,	0·9	,, ,,
,,	22nd	.	.	17·9	,,	,,	0·9	,, ,,

It appears that the riper the grape the more sugar it contains, and it produces a wine richer in alcohol, so that the grapes are never gathered until perfectly ripe. The grapes of the white vine are of a brown-yellow when ready for gathering for wine, and the red and blue grape must be extremely dark before the seed will separate from the fleshy part of the grape sufficiently for wine-making purposes.

The grapes are sometimes plucked, and sometimes left on the stalk. The separation of the grape from the stalk is effected either by hand or by the aid of a hurdle, the openings between the bars of which are only sufficiently wide to admit the passage of the grape, or by a wooden or brass trellis-work, or finally with a large wooden fork 0·5 to 0·6 metre in length. The stalk contains much tannic acid, and it is therefore necessary that all the grapes should be thoroughly separated before pressure; but in some cases, when the grape contains too little of this acid, a few stalks are purposely allowed to remain.

The Pressing of the Grapes.—After the grapes are stripped from the stalks, they are placed in a vat and stamped with a wooden maul or pestle to express the juice. They are generally allowed to remain for some time, and afterwards submitted to a second bruis-

ing, the maceration being for the purpose of softening the skins and fleshy part of the grape. The whole of the juice and grape-skins, or marc, is then put into a butt with perforated sides, through which the must trickles into the fermentation vat beneath. If a white wine is being operated upon, to prevent it becoming *stringy*, as the term runs, from an insufficient supply of tannic acid, small quantities of stalks are added from time to time. This addition renders the wine more easily clarified by the addition of white of egg or isinglass in a subsequent stage of the process. While the wine is in the vat, the fermentation is allowed to proceed, and the slight acidity generated reacts upon the colouring matter and aromatic constituents of the grape, these being taken up in the alcohol set free.

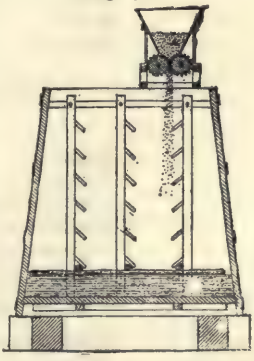
The wine-presses are of very various construction. The most general is the beam-press, roughly constructed with a pole 12 to 16 metres in length, and four to six oaken cross-beams. These presses have considerable power, but they are tedious to work, and soon get dirty. The lever-press is more efficacious, and is made in many forms, the pressure being mostly from below. The hurdle- or sledge-press is of the rudest kind, consisting merely of hurdles and rough heavy stones. The best presses are the screw-presses made of wood or cast-iron. 100 parts of grapes yield 60 to 70 parts of must. The ripest grapes yield the first juice in the press; the results of stronger pressure are more acid. The result of the first pressure is termed the wine or the first wine; then comes the press-wines; and finally the after-wines. The residue or marc is sometimes treated with water to obtain an inferior wine.

The Centrifugal Machine.—In 1862 Steinbeis, of Stuttgart, with the co-operation of Reihlen, endeavoured to express the juice of the grape with the aid of the centrifugal machine instead of the press. They were enabled in ten minutes to express the juice perfectly from 100 to 120 lbs. of grapes, including the time required to fill and empty the machine. In 1869, Ballard and Alcan obtained equally successful results, some of which were made comparative with those obtained by a good press:—

	Centrifugal Machine.		Press.
Must	79·141	...	77·086
Residue	20·214	...	18·601
Loss	0·645	...	4·313
	100·000	...	100·000

Perret fixes in a vat six pillars, each of which has six hooks pointing downwards (Fig. 505) at 25 centimetres apart. Six hurdles made of ribs placed 6 to 8 centimetres from each other are then put in the vat in such a manner that as it is filled they may rise only so far as the hooks of the pillars allow, thus preventing the skins, stalks, &c., from ascending. Upon the upper hurdle is laid a thin layer of straw in order to prevent any berries which may be carried up by the motion of fermentation from ascending to the top. When the wine is drawn off, the hurdles, with the dregs, &c., between them, sink to the bottom. The process deserves attention.

Fig. 505.



The Chemical Constituents of the Must.—Besides the stalk of the grape, there are the outside skin, the hull, the seeds, and the juice. Of the composition of all these substances, with the exception of the grape-juice, our knowledge is very deficient. Besides cellulose, the stalks contain much tannic acid, and an acid very sour to the taste. The hull of the grape contains the colouring matter and a small quantity of tannic acid. The seed contains a peculiar acid, œnanthic acid, and an ether, bearing the same name, to which the bouquet of the wine is due.

The Sugar of the Grape.—The wine grape contains more sugar than any other kind of grape. The quantity of sugar—a mixture of dextrose and levulose—is seldom less than 12 per cent., while it is sometimes as much as 26 to 30 per cent. The proportion of acid to sugar is in good years and in a good grape, according to Fresenius, 1 : 29; in average years and cases, 1 : 16; and when the proportion is only 1 : 10 the grapes are useless for the production of wine. The proportion between the acid and sugar in wine-must from the same kind of grape for different years is, according to this eminent chemist—

In a very inferior year,	1847, as 1 : 12
In a better year,	1854, as 1 : 16
In a good year,	1848, as 1 : 24

During the fermentation of the must, potassium bitartrate is deposited, and from this source most of the tartar of commerce is obtained. This salt is insoluble in dilute alcohol; consequently, as the sugar changes into alcohol it is thrown down. It is from the fact of containing tartaric acid, which, by combining to form an insoluble salt, is thus prevented exerting an unfavourable influence on the wine, that grapes possess so much more the property of making a good wine than do other fruits. The malic and citric acids contained in currants and gooseberries cannot be withdrawn in this manner. Hence the addition of sugar to wines made from these fruits to veil the acidity; the addition, however, giving rise to the danger of a second fermentation, and consequent acidity. According to Al. Classen, 1 kilo. of ripe grapes gave (in 1868) 577 to 688 grammes of juice; and 1 litre of juice contained—

Water	860 to 830 grammes
Sugar (dextrose and levulose)	150 „ 300 „
Pectin, gums, extractive matter, protein substances, organic acids, and mineral matters	30 „ 20 „
	1040 to 1150 „

1000 parts of juice of ripe (Rhine, 1868) grapes contained—

	1.	2.	3.
Solid matter	164·4	189·7	204·6
Sugar	149·9	162·4	174·0
Free acid	7·2	6·8	4·8
Ash	2·7	3·0	4·0

In 100 parts of the ash were contained—

	1.	2.	3.
Phosphoric acid	16·6	16·1	14·0
Potash	64·2	66·3	71·4
Magnesia	4·7	2·8	2·6

C. Neubauer (1868) analysed two kinds of grapes, and found—

	Neroberger (Large Grapes).	Steinberger (Selected Grapes).
Sugar	18·06	24·24
Free acid	0·42	0·43
Albuminous substances	0·22	0·18
Mineral constituents (potash, phosphoric acid, &c.)	0·47	0·45
Combined organic acids and extractive matter	4·11	3·92
Total of soluble constituents	23·28	29·22
Water	76·72	70·78
	100·00	100·00

The Fermentation of the Grape-juice.—The fermentation of the grape-juice is spontaneous—that is, it is consequent upon the exposure of the grape-juice to the atmosphere, without the addition of yeast. The albuminous matter of the must forms, under the influence of the atmospheric spawn, or yeast germ, the well-known fungus *Penicillium glaucum*, or yeast cells. The fermentation begins at a temperature of 10° to 15°, and is effected more or less rapidly according to the temperature. Too low a temperature will retard the progress of fermentation, as also will the addition of sulphurous acid; the same effect is obtained by the addition of other sulphur compounds, as, for instance, the essential oil of mustard, which contains allyl sulphocyanide. The must is left in open vats. Bubbles of carbonic acid soon appear, scum collects upon the surface of the juice, and an alcoholic odour pervades the wine at this stage. About the seventh day the fermentation commences to decrease, and about the tenth or fourteenth day the fluid begins to clear, no more carbonic acid or scum appearing. The yeast cells formed are carefully removed from the bottom of the vessel, and the wine run into casks, where it undergoes a slight after-fermentation. If there be much sugar contained in the grape, and a small quantity of azotised matter, the resulting wine will be sweet; but if the proportion of sugar be small and albumen large, a dry wine is the result.

Drawing-off and Casking the Wine.—After the principal fermentation, the greater part of the sugar of the must is found to be separated into alcohol and carbonic acid. There is still likely to arise, unless the temperature be considerably decreased, a fresh fermentation, known as the after-fermentation. Should this after-fermentation continue too long, vinegar is formed, and to prevent this the wine, after the disappearance of the bubbles of carbonic acid upon the conclusion of the principal fermentation, is at once "spigotted off" from the lees into casks, the object being to cut off communication with the atmosphere as much as possible. The casks are nearly filled, and are bunged loosely, being filled completely a day or two after. Wines casked in December will often continue fermenting till February or March. Strong wines rich in alcohol can be kept in cask until they have become quite clear; but weak wines must be soon bottled, as the oxygen of the air is liable to convert the hydrate of the oxide of ethyl, or alcohol, into trioxide of acetyl, or vinegar.

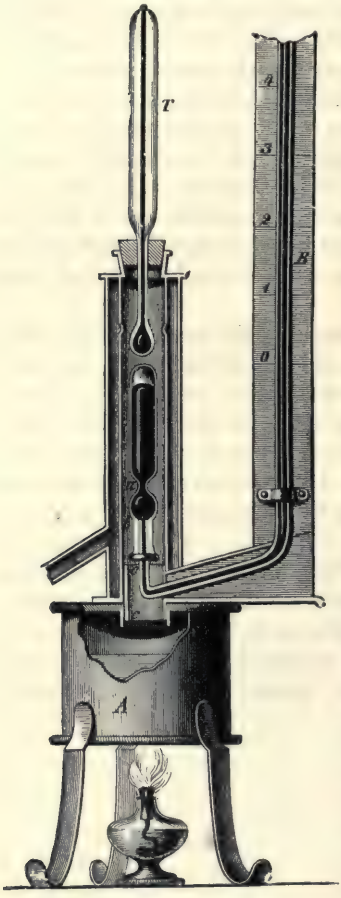
Constituents of Wine.—Constituents that were not found in the must are characteristic of the wine; the chief of these is alcohol. Succinic acid and glycerine, the constant products along with alcohol and carbonic acid of vinous fermentation, are also to be found. A "dry" wine, such as the French and Rhenish wines, is one in which all the sugar has been decomposed; a "sweet" wine, on the other hand, is one in which some sugar has remained undecomposed, either from an insufficiency of albuminous matter to nourish the yeast cells, or from the checking of the fermentation by exposure to a low temperature. A very sweet and thickly fluid wine is termed a "liqueur." The difference in colour is due to three substances—a blue colouring matter, a brown colouring matter, and tartaric acid. The brown colouring matter is present in all light or white wines, while the blue colouring matter, found in the skins of purple or black grapes, becomes in the wine a red colour, the change arising from the contact with the tartaric acid. Wines of the first year after growth are termed new or "green" wines. The average composition of wines, in 1000 parts, is the following:—

Water	900–891
Alcohol*	80–70
Homologues of alcohol (propylic, butylic alcohol)*	
Ethers (acetic, œnanthic)*	
Essential oils	
Grape sugar (dextrose and levulose)	
Glycerine*	
Gums	
Pectin	
Colouring and fatty substances	
Protein bodies	20–30
Carbonic acid*	
Tartaric and racemic acids	
Malic acid	
Tannic acid	
Acetic acid*	
Lactic acid (?)*	
Succinic acid*	
Inorganic salts	

Those substances marked (*) are formed during the principal fermentation.

The quantity of alcohol contained in a wine is due partly to the quantity of sugar and partly to the quantity of albuminous matter contained in the must. It is chiefly ethylic or ordinary alcohol. The specific weight of the wine gives only approximately the alcoholic contents. A better method of estimation is by means of an alcoholometer. Of these instruments, Geissler's vaporimeter is, perhaps, one of the best, in which the pressure exerted by the vapour of the wine upon a column of mercury gives a measure of the alcohol contained. The vapour of absolute alcohol at a temperature of 78·3° exerts a tension equal to that exerted by aqueous vapour at 100°. It is therefore only necessary to ascertain the height of the column of mercury and the temperature to arrive at the quantity of alcohol. The apparatus is shown in Fig. 506, and consists essentially of four parts—viz., (1) A brass vessel, *A*, half filled with water, heated by means of the lamp to the boiling-point; (2) A bent glass tube, *B*, to which a wooden scale is fixed; (3) A cylindrical glass vessel, *O*, filled with mercury and the wine to be tested; (4) A cylinder of sheet-brass, in the upper part of which a thermometer, *T*, is fixed. The glass vessel, *O*, is filled with mercury to the mark, *a*, and then completely filled with the liquid to be tested. The boiling-vessel is now affixed, the brass cylinder drawn over the mercury tube, and the thermometer inserted. Heat is applied, and the water raised to the boiling-point; the steam ascends into the brass cylinder, and heats the wine and mercury to the boiling-point of water. The wine expands, and is partly vaporised, forcing the mercury up the arm, *B*, which has been previously graduated by experiments with fluids of known alcoholic contents; the mercury of course rises the higher the more alcohol there is contained in the wine. The variable consti-

Fig. 506.



tuents of the wine, the extractive matter, &c., do not influence the result. The carbonic acid must have been removed previously by filtering the wine through freshly burnt lime. Equally good, if not better, results are, however, to be obtained by the distillation test, effected by distilling 10 c.c. of the wine, and adding to the distillate sufficient water to make a total of 10 c.c., the specific weight of the fluid giving the alcoholic contents of the wine. The alcoholometer most generally employed is the *ebullioscope* of Tabarié (Fig. 507). With the barometer at 760 mm. water boils

Fig. 507.

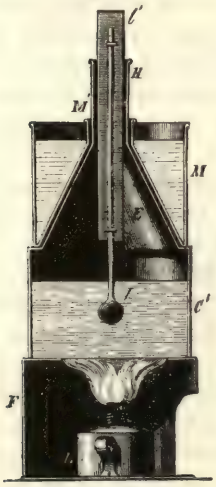
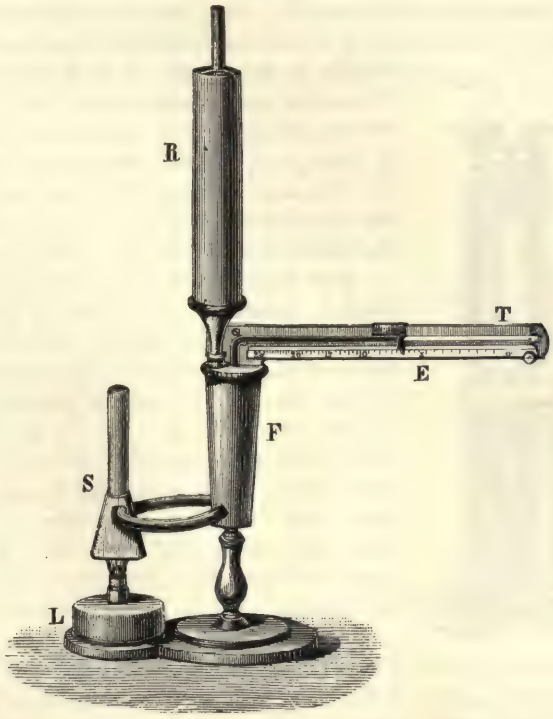


Fig. 508.



at + 100°, and alcohol at + 78·3° C. The nearer, therefore, the boiling-point of the fluid tested approaches 78·3°, the greater the alcoholic contents. The wine is poured into the vessel *C*, and the cover, *E H*, replaced. The fluid is heated by means of the lamp, *L*, and the steam ascends round the thermometer, *t t'*, the height of the mercury of which, when the fluid boils, varies inversely as the alcoholic contents of the wines tested. The vessel *M M'* is filled with cold water, to hasten the condensation of the vapours. If the boiling-point of pure water be taken at 99·4° C., the following boiling-points show the quantity of alcohol contained :—

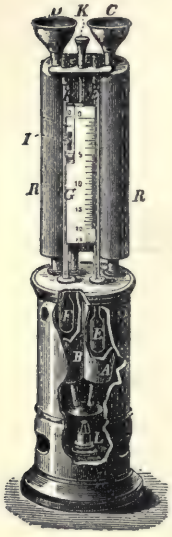
96·4° C.	3 per cent. alcohol	91·1° C.	9 per cent. alcohol
95·3 „	4 „ „	90·2 „	10 „ „
94·3 „	5 „ „	89·7 „	11 „ „
93·5 „	6 „ „	89·3 „	12 „ „
92·7 „	7 „ „	88·8 „	13 „ „
91·9 „	8 „ „	88·4 „	14 „ „

Latterly, the ebullioscope of Malligand and Vidal has come into use in France and Germany. It consists of a brass vessel, *F* (Fig. 508), of the form of a truncated cone, and is connected at its bottom with a vessel, bent in the shape of a ring. A lid, which can be screwed on, and which is provided with two apertures, closes the vessel

F perfectly air-tight. One of the apertures receives the refrigerator, *R*, and the other the thermometer, *T*. The thermometer is horizontal, and is provided with a scale, upon which the vol. percentages of alcohol are shown, from 0° to 25°. The boiler is first filled with water, which is heated to boiling by the spirit-lamp, *L*, and the thermometer is read off. Boiling-point answers to the nul of the alcoholic scale. The vessel is then filled with the wine in question up to a ring in the inside, and its proportion of alcohol is found by heating to the boiling-point. Wines very rich in alcohol are first diluted with an equal volume of water before being submitted to the experiment.

Amagat's ebullioscope (Fig. 509), in order to compensate for the height of the barometer, has, in addition to the wine-boiler, *A*, a similar boiler, *B*, for water. The pipes leading to the funnels, *C* and *D*, are surrounded by the coolers, *R*. When the instrument is to be used, 50 c.c. of the wine in question are introduced into *A* through the funnel *C*, and 15 c.c. water into *B* through *D*, and it is heated to a boil by means of the spirit-lamp, *L*. The thermometer *F* shows the boiling-point of water, according to which the scale *G* is fixed by means of the handle, *k*, so that the result can be read off on the thermometer *E*.

Fig. 509.



Red French wines contain 9 to 14 percentage by volume of alcohol; Burgundy, 9, 10, and 11 per cent.; Bordeaux, 10, 11, and 12 per cent. Other French wines contain 8 to 10 per cent.; the wines of the Palatinate, 7 to 9·5 per cent.; Hungarian wines, 9 to 11 per cent. Champagne contains 9 to 12 per cent.; Xeres, 17 per cent.; Madeira, 17 to 23·7 per cent. Acids exist in all wines, and are generally carbonic, succinic, tartaric, malic, and acetic acids; these acids are found partly free, partly combined as salts; tartaric acid, for instance, as *cremor tartari*, potassium bitartrate, and other acid tartrates. Fauré found an essential gum, which he termed œnanthin, and which, with glycerine—first shown by Pasteur in 1859 to be a normal constituent of wine—helps to give a certain consistency to the wine. Pohl found (1863) in Austrian wines 2·6 per cent. glycerine. As wine ages the glycerine disappears. The colouring matter of wine is of interest in the case of red wines only, as the yellow-brown colour of some wines is undoubtedly due to oxidised extractive matter. The colouring matter of red wines has received from Mulder and Maumené the name of œnocyanine, while it is commonly termed *wine-blue;* it is a blue substance similar to litmus, possessing the property of turning red in the presence of acids. It is insoluble in water, alcohol, ether, olive oil, and oil of turpentine; but soluble in alcohol containing small quantities of tartaric or acetic acid. With a trace of acetic acid the solution is practically blue, turning red upon the addition of more acid; neutralised with alkalies, the solution remains blue. On the evaporation of a wine to dryness the extractive matter remains, consisting of a mixture of non-volatile acids, the salts of organic and inorganic acids, with œnanthin, colouring matter, sugar, protein substances, and extractive matter, the nature of which is unknown. The quantity of extractive matter differs greatly, varying with the kind of wine and the degree of fermentation of the sugar. Fresenius found in Rhine wines a maximum of 10·6 and a minimum of 4·2 per cent. of extractives; Fischern, in the wines of the Palatinate, from 10·7 to 1·9 per cent.; in Bohemian wines, 2·26; in Austrian, 2·64; in Hungarian, 2·62 per cent. The mineral constituents of wines exist in but small quantities—as an average in old Madeira, 0·25 per cent.; in old Rhine wines, 0·12 per cent.; and in old ports, 0·235 per cent. Van Gockom, Veltmann, and Mösmann found in 1000 parts of wine—

Madeira	2·55 parts of ash
Teneriffe	2·91 „
Rhine wine	1·93 „
Port	2·35 „

Pohl estimated the following number of parts ash in 100 parts of wine:—

Bohemian	1·97 part	Slavonian	1·91 part
Croatian	1·68 „	Styrian	1·63 „
Carniola	1·81 „	Tyrol	1·84 „
Lower Austrian	2·00 parts	Hungarian	1·80 „

The ash contains potash, lime, magnesia, soda, sulphuric acid, and phosphoric acid.

The *Handwörterbuch der Reinen und Angewandten Chemie* (Bd. ix. Seite 676) gives the following analyses of wine-ash, the first four being by Crasso, and the fifth by Boussingault:—

Ash of Wine.	1.	2.	3.	4.	5.
Ash (per cent)	0·26	0·34	0·41	0·29	0·18
Potash	65·5	63·9	71·3	62·0	45·1
Soda	0·3	0·4	1·2	2·6	
Lime	5·2	3·4	3·4	5·1	4·9
Magnesia	3·3	4·7	4·0	4·0	9·2
Iron oxide	0·7	0·4	0·1	0·4	
Manganese oxide	0·8	0·7	0·1	0·3	
Phosphoric acid	15·5	16·8	14·1	17·0	22·1
Sulphuric acid	5·2	5·5	3·6	4·9	5·3
Silica	2·0	2·1	1·2	2·2	0·1
Potassium chloride	1·5	2·1	1·0	1·5	
Carbonic acid	—	—	—	—	13·3
	100·0	100·0	100·0	100·0	100·0

For the determination of glycerine in sweet wines 50 c.c. of the sample are mixed in a capacious flask with 10 grammes sand and slaked lime in powder and heated on the water bath until no more lime is dissolved, all the sugar is converted into sugar-lime, and the mass, after prolonged heating, has still a caustic smell. 100 c.c. of alcohol at 96 per cent. are gradually added, the whole is well shaken, the precipitate is allowed to settle, the largest part of it is decanted or passed through a flannel filter, the residue is twice washed with alcohol (filtered), the precipitate is rinsed upon the filter, drained, washed again if the filtrate is slightly yellowish, the alcohol is expelled from the filtrate, and the residue is treated like the first evaporation residue of a common wine.

Concerning the odoriferous constituents of wine, which often determine its value, nothing trustworthy is yet known. That compound which gives wine its peculiar odour is a mixture of œnanthic ether with alcohol. But, according to an investigation of Neubauer's, œnanthic ether is a compound of different substances, of which the most important are caprylic and capric ethers, and is a product of the fermentation of the must. The *bouquet* (German: *Blume*) is probably a mixture of ethers formed during fermentation, but which, on account of their extremely minute quantity, have not been distinguished and insulated.

Neubauer justly says in his *Chemie des Weines:* "Everything which art has yet done to imitate the aroma of wine, in spite of the enticing names by which it is advertised, is a miserable sham [*elendes Machwerk*]. Our chemical knowledge of the bouquet is extremely trifling, and science, with her present resources, is impotent as against the genii of wine."

The Diseases of Wine.—Wines are subject to various causes of deterioration, termed maladies, distempers, or diseases. That most commonly occurring is *ropiness or viscidity*, the cause of which was for a long time unknown. François showed that it

was due to the decomposition of the glucose into azotised matter and mannite, and at the same time indicated the proper remedy—the addition of tannic acid. He employs 15 grammes of tannin to 230 litres of wine. This is well mixed with the wine, which is allowed to stand for a few days. At the end of this time the tannin will have separated the azotised matter, and the wine may be bottled off.

The *souring* of wine is due to the conversion of the alcohol into acetic acid, caused, according to Pasteur, by the formation of the vinegar plant, or *Mycoderma aceti*, which he found in all sour wines. This disease is very common, and may result from too small a proportion of alcohol, too high a temperature of the cellars, or exposure to the atmosphere. The wine, if too far soured, is fit only for making vinegar; but slight cases can be remedied by an addition of sugar. The formation of vinegar may be somewhat delayed by impregnating the wine with sulphurous acid. In some cases the acetic acid may, by the addition of tartaric acid, be removed as acetic ether; but the acetic acid can never be neutralised with alkalies, as the salts formed are very easily soluble.

The *bittering* of wine, or its acquirement of a bitter flavour, is due to another cause, the formation of a bitter substance, which develops as the wine ages, or at too high a temperature. Maumené suggests as a remedy the addition of slaked lime in the proportion of 0·25 to 0·50 gramme per litre. Bittering is due also to the formation of brown aldehyde resin. *Mould* in wines appears as a white vegetable (fungus) film covering the surface, and arises from an insufficiency of alcohol; consequently, weak wines are more subject to this malady. The film of mould should be removed and the wine used as soon as possible, for wine affected with this disease soon turns sour. The *decaying* of a wine is due to the dissipation of the alcohol and the decomposition of the acids of the wine; the wine obtains an astringent taste and a dim, thick colour, finally turning sour. The potassium bitartrate is converted into potassium carbonate, affecting the colouring matter, and tannic acid, which pass over into humus substances. At the commencement of this decomposition a remedy may be found in the addition of a small quantity of sulphuric ether. *Caskiness*, or the taste of the cask, due to an essential oil formed in casks that have long stood empty, is best removed by the addition to the wine of a small quantity of olive oil, and agitation; the olive oil absorbs the essential oil, and brings it to the surface of the wine, whence the oily matter may be skimmed, or the wine may be filtered through freshly burnt charcoal. All casks and vessels that have stood long empty should be well steamed before use.

Pasteuring.—Pasteuring, a term which usage has substituted for pasteurisation, or the conservation and artificial ageing of wines, according to Pasteur's method, is a great improvement in the general treatment of wines to ensure their keeping. It consists essentially in heating the wine to 60° C., and for this purpose the apparatus designed by Rossignol is best suited. A metal cask, T' (Fig. 510), contains at the bottom a copper vessel, C, with a trumpet-shaped cover extending in the open tube, c, above the top of the vessel T; t is a thermometer. Water is poured into the vessel, C, until the tube c is three parts full. The wine is placed in the metal cask, T, and, by means of the tap, r, and the tube f, run off into the cask F, when sufficiently heated. The water in the copper vessel, C, is employed to prevent the direct heating, by the flame, of the vessel containing the wine, and the consequent burning of any insoluble matter settling to the bottom of the vessel. Fig. 511 shows in detail the manner of fastening the vessels together. A copper ring, a, encircles the vessel T, and beds with the walls of this vessel into the india-rubber band, d, into which it is pressed by the tightening of the bolts, e, binding the ring of angle-iron and lower iron ring, b, together. The joint is thus rendered water-tight. The vessel T is not quite filled with wine, to allow for expansion under heat; by this means the wine is exposed to a

known quantity of air. Wine should not be artificially aged in contact with air, as Pasteur has proved that such processes deteriorate the colour and the flavour of the wine; and in ordinary cases, where part of the process of ageing consists in heating the wines for a short time in an open vessel with a full exposure to air, the wine acquires a peculiar boiled flavour, *goût de cuit*, easily recognisable by the connoisseur. By Pasteur's method, however, neither the flavour nor the colour of the wine is deteriorated; indeed, the latter is improved by the expulsion of the carbonic acid.

Pasteur has shown that most of the diseases of wine (acetification, ropiness, bitterness, and decay or decomposition) are due to the growth of different ferments, consisting of minute vegetable cells, always existing in wines, and becoming active and destructive under certain conditions, such as change of temperature and oxidation. He recommends* that these plants or fungi should be *killed*, as the best means of ensuring the keeping of the wine, and the particular *modus operandi* selected is essentially the following, differing considerably from the foregoing method. The bottles are quite filled, the wine touching the cork, which is inserted with such a degree of firmness that the wine in expanding may force the

Fig. 510.

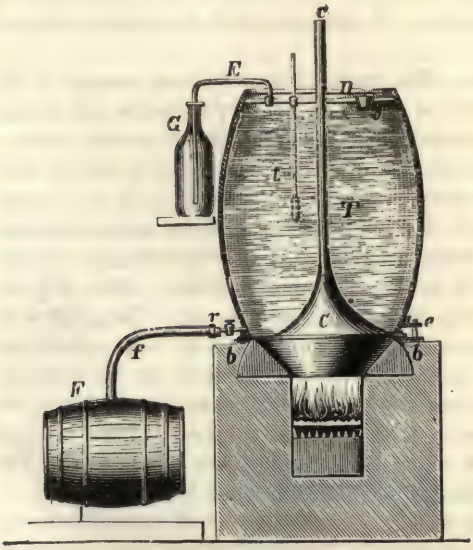


Fig. 511.

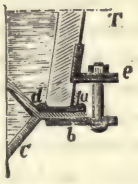


Fig. 512.

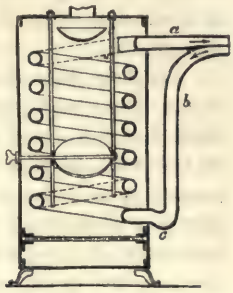


Fig. 513.



cork out a little, but not so much as to admit air into the bottle. The bottles are then placed in a chamber heated to 45° to 100°, where they remain for an hour or two, after which they are removed, set aside to cool, and the cork driven in. By this means the life or active principle of the fungi is destroyed, while the wine acquires an increased bouquet, is of a more beautiful colour, and, in fact, is to a considerable extent aged. Both new and old wines can be thus treated.

For heating wine in its own casks, Ballo proposes an apparatus, the hygrothermant. The liquid, heated in the spiral, ascends through the tube, *a* (Fig. 512), into the cask, and cold wine enters in its place through *b*. The circulation begins with the smallest difference in temperature between *a* and *b*, and lasts to the boiling-point. The apparatus depends on the principle of heating by hot water. The novelty here is that the cold- and hot-water pipes, on their exit from the source of heat, unite to a single tube in which the two opposite currents are separated by a thin metal partition. The form of the pipe is shown in Fig. 513.

* *Comptes-Rendus*, May 1, 29; August 14, 1865.

Clearing or Fining the Wine.—Most wines are self-clearing, the ferment settling to the bottom of the cask, and leaving the wine clear and pure. This applies chiefly to dry wines, which have less sugar than sweet wines. The sweet wines are generally more thickly fluid on account of the quantity of sugar they contain, and consequently more frequently need clearing. Fining, as it sometimes called, or clearing, consists in adding to the muddy wine some albuminous or similar substance that will mix with the suspended matter and carry it to the bottom or bring it to the surface of the wine. The substances most generally employed are white of egg, ox-blood, and milk, or mixtures of these substances. "Plastering," or the addition of gypsum to the must, is said to improve the colour of red wines, and, by taking up water, it increases the relative proportion of alcohol, which retards the fermentation, and thus gives more time for the extraction of colouring matter. It converts the soluble potassium salts into insoluble lime salts and potassium sulphate. As the plastered wine contains potassium sulphate in quantity and remains saturated with gypsum, wine thus treated has probably unpleasant and injurious effects on the human organism; the addition of gypsum to wine is to be unconditionally condemned.

Hugounenq recommends, instead of gypsum, an addition of calcium diphosphate as a clarifying and preservative agent. "Phosphatage" is said to have all the good effects of plastering without increasing the proportion of sulphates and diminishing that of phosphates.

Residues from the Production of Wine.—The waste of wine making consists of the stems, husks, and seeds of the grapes, as well as of the fermentary sediment and tartar. Both descriptions of waste find numerous applications. The lees left from the pressing of the wine contain a not unimportant quantity of must, which (1) is employed in preparing an inferior wine; (2) in the making of an inferior brandy; (3) in the preparation of verdigris (see page 458); (4) in vinegar making, and for promoting the formation of vinegar from saccharine or alcoholic fluids. (5) In wine-making countries the lees are much employed as fodder for horses, mules, and sheep; while (6) the residue of the after-pressing or final pressing is used as manure. (7) The grape seed yields an oil in quantities of 10 to 11 per cent., or (8) tannic acid in large quantities. The oil can be extracted by pressure or by treatment with benzole, or with carbon disulphide. The tannin obtained can be employed for the preservation of hides, &c. (9) Potash is prepared from the calcined lees. (10) The stalks and seeds when calcined are employed in the preparation of a black colouring material (vine black). (11) The ferment and stalks are in some wine-producing countries, besides being employed in the preparation of tartar and potash, also used in the distillation of a peculiarly rich brandy, in which an oil is found possessing highly the flavour of cognac, and known in commerce as wine oil, cognac oil, *huile de marc.* (12) Crude tartar is found with calcium tartrate, colouring matter, and yeast, forming a more or less thick crust on the walls of the wine cask or in the crust deposited in the wine, but not firmly attached to the vessel, and is the chief source of the pharmaceutical potassium bitartrate ($C_4H_5KO_6$) and tartaric acid.

Effervescing Wines.—Effervescing wines have been known for many centuries. Some of Rembrandt's paintings exhibit, among the accessories, a champagne glass with effervescing wine. And from Virgil—

"Ille impiger hausit,
Spumantem pateram"—

it would appear that this description of wine was known to the Romans. In 1870 there were in Germany fifty producers of effervescing wines, with a production of $2\frac{1}{4}$ to $3\frac{1}{2}$ millions of bottles, $1\frac{1}{4}$ million of which were exported. In France the production amounts yearly to 16 to 18 millions of bottles.

All wines are capable of being produced as effervescing wines if bottled before the

fermentation is over. By bottling at this period the carbonic acid is retained in the wine, and, when the bottle is opened, the disengagement of the gas causes the appearance of effervescence. In this country the effervescing wine most generally known is champagne; but hocks, Moselles, and even red wines are very admirable when thus treated. If the wine contains much sugar, the fermentation is arrested in the bottle before all the sugar is consumed, producing a sweet effervescing wine. On the other hand, if the sugar is all exhausted in producing the carbonic acid, the result is a dry effervescing wine. These wines are very agreeable to the palate, and may be supposed to assist the digestion of the food with which they are taken; but, when new, they are dangerous, as being likely to communicate their state of change to the contents of the stomach, interfering seriously with digestion, and producing what is well known as "acidity." Dry effervescing wines are less likely to disagree than sweet wines of this class containing much sugar and fermentable matter. The connoisseur places great reliance in his judgment of a champagne upon the loudness, or rather sharpness, of the report when the cork is drawn, and upon the "bead" or bubble formed on the side of the glass by the carbonic acid gas. These effects are not proportionate, for while a loud report results from an extended fermentation, a good bead may be obtained with a very weak fermentation. The gas in a bottle of champagne exerts a pressure of some 5 atmospheres, and it will at once be evident that if the bottle be made a little smaller, reducing the space between the cork and the wine only one-twentieth, a considerable increase in loudness of the report will ensue.

The process of manufacturing effervescing wines is in general the following:—The best grapes are used for this purpose; for champagne, the black grape, called by the French *noirien*, is employed. The juice is expressed from the grape as soon after gathering as possible, in order to prevent the colouring matter of the skin affecting the wine; while the fruit is pressed as quickly and as lightly as possible. The juice from the second and third pressings is reserved for inferior, or red-tinted effervescing wines. The expressed juice is immediately poured into tuns or vats, where it is left to stand for twenty-four to thirty-six hours. In this time any earthy matter or vegetable impurities will have settled, and the juice is ready to be transferred to the fermenting vats, where it remains for about fifteen days. It is then put into casks, which are securely bunged; sometimes brandy is added in the proportion of one bottle to one hundred bottles of juice or must. Towards the end of December the wine is fined with isinglass, and a second time in the ensuing February. About the beginning of April the clear wine is fit for bottling. It now contains, if a good wine, 16 to 18 grammes of sugar, 11 to 12 per cent. of the volume of alcohol per bottle, and an equivalent to 3 to 5 grammes of sulphuric acid in free acids.

Great care is necessary in the manufacture of champagne bottles; they must be free from flaws, and made of pure materials. Generally each bottle is from 850 to 900 grammes in weight, and equal in thickness throughout. Formerly the flawed bottles amounted to 15 to 25 per cent., but recent improvements in manufacture have reduced the percentage to 10. Before the wine is introduced, the bottle is rinsed with a liqueur of white sugar-candy 150 kilos., wine 125 litres, and cognac 10 litres, the liqueur being allowed to remain in the bottle: according to F. Mohr, the cane sugar of the liqueur becomes converted into grape sugar in the champagne. It is doubtful whether glycerine might not be advantageously substituted for a portion of the sugar of the liqueur. The liqueur employed varies with the flavour of the wine: port, Madeira, essence of muscatels, cherry water, &c., are used, but rarely unmixed with some other favourite solution of the manufacturer, as, for instance, water 60 litres, saturated solution of alum 20 litres, tartaric acid solution 40 litres, tannin solution 80 litres. About 2 litres of this mixture would in practice be added to a butt of wine. The bottles are filled by

women, the proportion of liqueur introduced being about 15 to 16 per cent. of the wine. A space of about 2 to 3 inches is left between the wine and the cork, which, after being thoroughly moistened, is next inserted by a machine. The bottle is then passed to a man, termed in the French establishments the *maillocher*, who drives the cork home with a mallet. Another process, now generally effected by the aid of a machine, is the "wiring" or securing the cork with wire or string. The bottles are now conveyed to a cellar, where they are laid in horizontal racks against the wall. In about eight or ten days a deposit, termed "griffe," is formed, and shows that the time has arrived for the wine to be transferred to the cellar where it is to remain until sold to the merchant. The deposit is allowed to form during the summer, and in the ensuing winter means are taken for its removal. The bottles are well shaken, and placed with their mouths downwards, to cause the deposit to settle on the cork. The cork being removed, the sediment falls out, when more liquor is added, and the bottle re-corked and again wired. The bottle is now laid upon its side at an angle of about 20°, and in about eight to ten days the inclination is gradually increased until the vertical position is attained, when, by a dexterous movement of the cork, the gas is permitted to force out the remaining sediment. This process is repeated as many times as may be necessary, until the wine is perfectly clear. Wine thus prepared, generally known as sparkling wine, *vin mousseux*, is ready for the consumer at the end of from eighteen to thirty months, the time varying with the temperature of the season. One of the greatest causes of loss is the bursting of the bottles, sometimes as much as 30 per cent. of the wine being wasted. This in some measure accounts for the dearness of these wines.

By the analysis of several sparkling wines (1867 and 1870) the following results were obtained:—

	1.	2.	3.	4.	5.	6.
	Per mille.	Per mille.	Per mille.	Per mille.	Per mille.	Per mille.
Free acid	5·300	5·900	7·300	7·800	6·200	6·500
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Alcohol	8·400	9·500	8·500	8·400	9·800	8·400
Sugar	8·200	4·300	6·900	9·100	7·500	5·400
Extractive matter	11·600	7·500	9·800	12·000	11·600	15·200
Specific gravity	1·036	1·029	1·039	1·046	1·039	1·041

No. 1 came from Chalons; Nos. 2, 3 and 4 from Würtzburg, 2 being for export to India; 3 being the manufacture of J. Oppmann, and 4 of Silligmüller, both well-known German firms. No. 5 came from Sotaine & Co., of Rheims, and 6 from a well-known Rhenish firm, glycerine being substituted for a portion of the sugar.

Improving Wine Musts and Artificial Wines.—The worth or character of a wine is determined by its aroma and the amount of alcohol and free acid contained—decreasing with an increase of the latter, and increasing with increase of the former. The proportion between the chief constituents of the grape-juice, sugar, acid, and water, is nearly equal in all good wines, and this proportion is never accidental, but always belongs to a good wine. The grapes not fitted for making good wines are treated in two ways: either the expressed juice is allowed to ferment as it is, in which case an inferior wine is obtained; or, by the study of chemical analyses of good wines, the incomplete constituents are supplied, and others injurious to the wine removed, to make the must of that quality which will yield a good wine. The following are the best methods of improving the must:—

1. The addition of sugar to wine poor in this constituent, and the neutralisation of an excess of acid by means of pulverised marble (Chaptal's method).

2. The addition of sugar and water to must poor in sugar and rich in acid (Gall's method).

3. Repeatedly fermenting the husks with sugar-water (Petiot's method).
4. Removing the water by means of freezing, or by treatment with gypsum.
5. Removing the acid by means of a chemical reaction.
6. Addition of alcohol to poor wines.
7. Treating the prepared wine with glycerine (Scheele's method).

The addition of sugar to must poor in this constituent is the oldest method of improvement, and appears to have been known to the Greeks and Romans. At that time cane sugar was unknown, honey being used for sweetening purposes, which, being added to the wine, gave it a peculiar flavour, and rendered it thick. In years when honey was scarce, we are informed that the wine was inferior. Chaptal, in 1800, wrote a work on the cultivation of the grape, in which he gives a recipe for adding sugar to an inferior must, to render the wine equal to that of better years, the acid being neutralised with pieces of marble. In Burgundies, Chaptal's method is not much required to be used, as these wines rarely contain more than 6 parts per 1000 of free acid. The amount of pulverised marble (calcium carbonate) required to neutralise 60 parts of free acid is, as a rule, 50 parts; and the amount of sugar to be added, when the acid is in excess, is 100 parts for each 50 parts of alcohol required after fermentation, it being found that 15 per cent. of sugar in the must produces 7·5 per cent. of alcohol in the prepared wine. Thus, should it be desired to heighten the alcoholic contents from 7·5 to 10 per cent., 50 kilos. of sugar are added to every 1000 kilos. of must.

The cause generally of the poorness of the must in sugar is a wet or cloudy season, during which there has been but little warmth from the sun to ripen the grapes. Most German wines show, besides a lack of sugar, a superabundance of malic and tartaric acids; and while the addition of a sugar solution increases the alcoholic contents, it does not remove these acids, which impart a flavour to the wine and lessen its worth. The addition of saccharine solution does not, as might be expected, enfeeble the bouquet of the wine if pure starch sugar, containing no dextrine, be employed. The use of impure starch sugar causes a quantity of unfermented matter to remain in the wine, imparting to it a tendency to decay. Gall's method is found to be economical, as a flavouring material can be added to very inferior must. According to Gall, a normal must should consist of—

Sugar	24·0 per cent.
Free acid	0·6 „
Water	75·4 „
	100·0

1000 kilos. of such a must contain, therefore, 240 kilos. of sugar, 6 kilos. of free acid, and 754 litres of water. If, by analysis, the must to be improved yields only 16·7 per cent. sugar and 0·8 per cent. acid, there are to be added 153 kilos. of sugar and 180 kilos. or litres of water, by which addition 1333 kilos. of normal must are obtained, corresponding to an increase in quantity of 33 per cent.; while in some years, when the acid contents are as much as 12 to 14 per cent., the increase in quantity rises to 100 to 115 per cent., but seldom more.

Petiot based his method on the fact that, according to the usual process of preparing the must, the colouring and bouquet constituents remaining in the marc are sufficient to give the flavour and odour of wine to a lixivium of sugar-water. This method may therefore very justly be considered as yielding a wine without the aid of grape-juice. To the marc left after the expressure of the grape-juice cold water is added, equal in quantity to the must removed: in this water the marc is allowed to macerate for two to three days. The water takes up the various soluble constituents of the marc; after the time specified the liquor is removed, and the amount of sugar

and acid it contains ascertained. There is usually only 2 to 3 per cent. of sugar; consequently, an addition of 17 to 18 per cent. must be made; and if there should be too little acid, tartaric acid must be added to approximate to the acid contents of a normal must. The artificial must, as it may be considered, is then put into the fermenting vat, while the marc is again treated in a similar manner, a longer immersion being this time required. The resulting wines are darker in colour than wines prepared from the natural must, in consequence of a larger proportion of tannin. The flavouring of these wines is a matter of experience, and does not fall under any chemical consideration.

Freezing is employed in the improvement of wine, for the purpose of reducing the aqueous contents. According to the experiments of Vergnette-Lamotte and Boussingault, the effect of cold upon wine is of a very complicated nature. By cooling the wine at a temperature of 0·6° there first occurs the precipitation of those substances that are insoluble at this temperature. These consist of cream of tartar, colouring matter, and nitrogenous substances, and a fluid possessing the property of becoming solid at 6°. When these substances are removed the wine becomes more ardent, richer in alcohol, and its peculiar merit is that it is not liable to after-fermentation, and can be kept in vats and half-empty casks. The removal of the acid from wine is effected best by means of calcium carbonate (pulverised marble, chalk), sugar of lime, or neutral potassium tartrate. An addition of calcium carbonate to the must, or to the wine, is not detrimental, in so far that the wine retains none, or a very small quantity, of the lime-salt. Calcium carbonate will not be of service in the case of so-called acid fermentation, as calcium acetate will then be formed, and the wine is no longer worthy the name. Liebig recommends the use of neutral potassium tartrate for this purpose, as potassium bitartrate is formed, which settles as an insoluble salt on the sides of the vessel or bottle. The use of this neutralising agent has the merit, moreover, of not injuring the flavour and odour of the wine. Sugar of lime can be employed in the case of wines not containing acetic acid. To prepare the sugar of lime, slaked lime is diluted with ten times the quantity of water, to form a thin cream. This cream is thinned with sufficient water to obtain a milk of lime, in which sugar-candy is dissolved. The solution is left to stand, and the clear supernatant liquor—a solution of sugar of lime—decanted to mix with the wine as required. When the wine is treated with the sugar of lime solution, the lime forms with the acid of the wine an insoluble salt, which is precipitated, while the sugar remains in the wine.

Another addition to wine, hardly bearing upon its improvement, but effected as a means for its preservation during removal or exportation, is that known in France as the *vinage*, a certain quantity of brandy being mixed with the prepared wine. When the wine is to be exported from France, the law permits the addition of 5 litres of brandy to each hectolitre of wine, provided the alcoholic contents after the addition do not exceed 21 per cent. But experiments have proved that the wine delivered to private consumers does not on the average contain more than 10 to 11 per cent. of alcohol, while the wine delivered to retail firms averages 16 to 17, and to wholesale firms 22 to 24 per cent. To prevent this fraudulent proceeding, the operation of vinage is permitted only in the Departments of the Pyrénées-Orientales, Aude, Hérault, Garde, Bouches-du-Rhône, and Var, immediately under the inspection of the Commissioners appointed to this duty. In 1865 Scheele introduced his method of improving wine by the addition of glycerine, the addition being made after the first fermentation has subsided. The limits of the addition lie between 1 to 3 litres of glycerine to 1 hectolitre of wine. But the expense will not permit of extended operations.

It is to be remarked that if a must is sweetened with starch sugar, a substance (dextrine) is introduced which is absent in natural wines [and which probably prevents the formation of a fine aroma, doubtless the reason why malt vinegars are deficient in the odour and flavour of wine, fruit, and cane-sugar vinegar].

Cider.—A must obtained from apples contained before and after filtration in 100 c.c.—

	Must (Filtered).		Cider.
Alcohol	—	...	5·800 centimetres
Extract	16·250	...	2·360 grammes
Ash	0·350	...	0·310 gramme
Malic acid	0·330	...	0·310 „
Acetic acid	—	...	0·080 „
Sugar	12·500	...	0·750 „
Pectin	0·620	...	trace
Lime	0·025	...	0·024 „
Magnesia	0·018	...	0·018 „
Potassa	0·106	...	0·105 „
Phosphoric acid	0·024	...	0·022 „
Sulphuric acid	0·009	...	0·680 (?)
Glycerine	—	...	0·680 „

Tartaric and citric acids were absent. Hence cider is distinguished from grape wine merely by the complete absence of tartaric acid and the corresponding larger proportion of lime. The same feature distinguishes gooseberry, currant (*Ribes*), and other fruit wines. If a moderate proportion of tartaric acid is added to cider the product cannot be distinguished from wine.

APPENDIX.—A. Rommir finds that an active ellipsoidal ferment, if introduced into grapes when crushed at temperatures below 21°–22°, multiplies more rapidly than the spores of the ferments found on the skins of the grapes. If a small quantity of an ellipsoidal ferment is added to grapes at temperatures above 21°–22°, the ferment added develops along with the natural ferment, and modifies the bouquet of the wine. R. Martinand has made an *experimentum crucis* which seems to confirm the author's theory. He divided the grapes of one and the same vine into five lots, and added to each lot a different ferment—to (1) that of a must of cherries in full fermentation; (2) of Beaujolais; (3) of Burgundy; (4) of champagne; (5) of Bordeaux. All these wines presented distinct flavours.—*Chemical News*, vol. lxi. p. 277.

BEER BREWING.

By beer, in the ordinary meaning of the word, we understand a spirituous liquor still in the state of secondary fermentation, obtained from germinating amylaceous seeds, chiefly barley (or wheat, latterly also rice), and hops, water, and yeast, by fermentation, but without distillation. According to the views of the German Brewers Association and the International Medical Congress at Brussels (1874), with which the conclusions of the Imperial Sanitary Department coincide, only liquors brewed from cereals and hops, fermented, but still in a state of secondary fermentation, have a right to be regarded as beer.

Materials for Beer Brewing.—The materials of beer brewing are:—(1) Grain, or amylaceous substances; (2) hops; (3) a ferment; (4) water.

The Grain.—The grain selected for this purpose is generally barley, as containing the proportion of sugar and starch best adapted to form alcohol. Many substitutes have been suggested, but with less success. In Bavaria, the large *double* barley (*Hordeum distichon*) is preferred. According to Lermer, 100 parts of dried barley contain—

Starch	68·43
Protein substances	16·25
Dextrine	6·63
Fat	3·08
Cellulose	7·10
Ash and other constituents	3·51

The ash of barley contains in 100 parts—

Potash	17
Phosphoric acid	30
Silicic acid	33
Magnesia	7
Lime	3

with other constituents. Potatoes, rice, maize, glycerine, and potato or starch sugar are employed in some modern breweries.

A good barley for brewing should be rich in starch, so that, when malted and converted into wort, it may give the highest proportion of extract. It must have a thorough germinating capacity, swell uniformly, and grow uniformly and rapidly if it has to produce a good, sound malt. The starch of the barleycorn should dissolve uniformly and rapidly; it must be free from mould and bacteria, perfectly inodorous, and in the subsequent operations it must communicate to the wort and the beer no substances of a bad smell or taste. The nitrogen must not exceed a certain limit. Märcker found in the highest quality of barley from the Saale an amount of proteine not exceeding 9 or 9½ per cent. 100 barley grains weigh from 3 to 5·26 grammes. The best barley contains 6½ per cent. of husk; other qualities up to 24·2 per cent.

Barley for distilling must have coats of a very uniform thickness. It should have a high percentage of proteine, which is converted into diastase, capable of transforming starch into maltose and dextrine.

For judging the quality of a barley for brewing a high germinating power is required. A good barley should have a germinating power of from 88 to 90 per cent. The barley should also grow uniformly. The weight of the grains and their degree of clearness should also be regarded. A germinating bed is prepared as follows:—Fine sand, which has been previously ignited, is laid upon a plate so high as to touch the upper margin of the cavity of the plate. So much water is added that the sand on shaking moves loosely. So much more sand is then sifted evenly over the surface as to stiffen the whole. The sand is then smoothed off level with the edge of the plate, and, after sowing, it is covered with a second plate.

Hops.—The hop (*Humulus lupulus*) is a diœcious plant of the natural order of *Urticaceæ*, the female flowers of which, or catkins, are used for flavouring beer. The catkins, or strobils, are composed of a number of bracts or scales, which are green, afterwards changing to a pale yellow. At the base of each flower is seated the pistil containing the seed, while surrounding the pistil are a number of little grains, embedded in a yellow powder, the farina, containing the active property of the hop, essentially lupuline, the grains being termed lupulinic grains. This yellow pulverulent substance contains an essential oil, tannic acid, and mineral constituents. The essential oil, the flavouring principle of the hops, is found, in air-dried hops, to the amount of 0·8 per cent.; it is yellow-coloured, with an acrid taste, without narcotic effect, of a sp. gr. = 0·908, turning litmus-paper red. It requires more than 600 times its weight of water to effect a solution. It is free from sulphur, and belongs to the group of essential oils characterised by the formula C_5H_8, and can become oxidised under contact with the air into valerianic acid ($C_5H_{10}O_2$), this oxidation being the cause of the peculiar cheesy odour of old hops; it is a mixture of a hydrocarbon, C_5H_8, isomeric with the oils of turpentine and rosemary, with an oil containing oxygen, $C_{10}H_{18}O$, having the property of oxidation alluded to. Tannic acid is found in the several kinds of hops, in quantities varying from 2 to 5 per cent., and is an important constituent, as it precipitates the albuminous matter of the barley and serves to clear the liquor. It gives with the per-salts of iron a green precipitate; treated with acids and synaptase, it does not separate into gallic acid and sugar; and by dry distillation it does not give any pyrogallic acid. The *hop resin* is the important constituent of the hops, and contains the bitter principle or lupuline. It is difficultly soluble in water, especially in pure

water, and when the lupuline or essential oil is absent. But water containing tannic acid, gums, and sugar dissolves a considerable quantity of the resin, especially when the essential oil is present. It is intensely bitter in taste, and becomes foliated when exposed to the atmosphere. Hop resin and the essential oil are not identical; the former is soluble in ether, the latter is not. In the course of long exposure it becomes insoluble. The gum and extractive colouring matter are of little use. The mineral constituents of hops dried at 100° are—9 to 10 per cent. ash, 15 per cent. phosphoric acid, 17 per cent. potash, &c.

Quality of the Hops.—The quality of the beer is almost proportionate to the quality of the hops. A rich soil is required for the growth of the hop-plant, well exposed to the influence of the sun's rays, and protected from easterly winds, which are highly detrimental. The hops must on no account be gathered until the seed is perfectly ripe, as it is only then that the bitter principle is fully developed. The ripeness of the hops can be ascertained by rubbing them between the fingers; if an oily matter remains, with a strong odour, they are fit for gathering. When gathered, the next most important operation is the drying, which is effected in kilns or stoves, at a temperature of 40°, with a good ventilation. When sufficiently dried, the small stem attached to the flower snaps readily. The temperature must be carefully regulated: not permitted to range so high as to run the risk of burning the hops, nor allowed to fall so low that the hops may afterwards become mouldy from under-drying. When dried, the hops are carefully packed, the finer kinds being put into canvas pockets, and the inferior into hop-bags of a coarser texture. The bags are then subjected to slight pressure in a hydraulic or screw press, to render them more impervious to air. To preserve the hops they are sometimes sulphured, that is, subjected to the action of vapours of burning sulphur, 1 to 2 lbs. of sulphur being employed to 1 cwt. of hops. Old hops are sometimes treated in this manner, to impart the colour and appearance of freshly dried hops, but the fraud can be detected by the odour. A good method of testing for sulphur in hops is as follows:—A sample of the hops is placed in a sulphuretted hydrogen apparatus, with some zinc and hydrochloric acid; the disengaged gas is passed through a solution of acetate of lead. If the hops contain sulphurous acid, sulphuretted hydrogen will be disengaged ($SO_2 + 2H_2 = SH_2 + 2H_2O$), and lead sulphide will be thrown down from the lead solution. Another, and still better, method is to receive the disengaged gas in a solution of sodium nitroprusside, to which a few drops of potash-lye have been added; the slightest trace of sulphuretted hydrogen imparts a beautiful purple-red colour to the solution.

Substitutes for Hops.—Attempts have been made to substitute quassia, walnut leaves, wormwood, gentian, extract of aloes, colchicum, and picric acid for the hop. None of these substances are efficient substitutes for the hop, though they impart a strong, bitter flavour. Three of them may be considered as poisonous. There was no foundation for the report that the seeds of a species of strychnos (and even ready prepared strychnine) were used in brewing bitter ales.

The water used in steeping the barley, extracting the malt, and mashing has a great influence upon the quality of the beer. A pure, soft water, or, at the most, one very slightly hard, is best suited for the purposes of the brewer.

Water contaminated with decomposing organic matter is especially objectionable. Such substances cling to the barley, continue to decompose on the softening floor, occasion mouldiness and putridity, and, under some circumstances, interfere with the fermentation of the wort obtained from such malt. Tannic, crenic, and apocrenic acids have an injurious action; hence water from woodlands, and that of rivers which receive the waste of tanneries, are to be used, if at all, with caution. Beer made with water containing animal impurities will not keep. The entrance of the waste waters of the brewery is often manifested by disturbance in the process of fermentation.

Lintner points out that the water used for softening the barley and filling the casks should contain little organic matter, and especially no ferment organisms. As regards the primary decomposition products, ammonia and nitrous acid, Lintner remarks that as we justly view with suspicion water containing such impurities, and reject it for dietetic use, so also in malting and brewing it should be used only in extreme cases and with great caution. A malting-house which used such water for softening had always to contend with mouldiness in the malt, which disappeared as soon as it was found possible to get a better supply of water. Water containing calcium carbonate is good for malting; calcium and magnesium chlorides, gypsum, and iron are injurious.

The brewing of beer may be considered to consist of the following operations:—

(1) The malting.
(2) The mashing.
(3) The fermentation of the beer-worts and the fining, ripening, and preservation of the beer.

1. *The Malting.*—Malting is the process during which the grain—barley—is germinated, by means of steeping in water until it swells and becomes soft. The non-germinated grain possesses only in a very small degree the property of changing its starch into sugar (dextrose); this property is very fully developed during the germination, so much so that it would be an easy matter to distinguish between the germinated and non-germinated seed by the degree of this property alone. As has been already stated, barley is the grain preferred, on account of its forming sugar in larger quantities than any other kind of grain. The germination of the seed takes place in three well-marked periods. In the first, the seed is enveloped in an outer organ, which becomes exhausted and withered. In the second, the growth of the germ is shown by the swelling at the end by which it was attached to the stalk; and in the third period, the little plumule, or *acrospire*, which would form the stem of the new plant, is put forth. The germinating seed is similar to an egg, with its white, yolk, and embryo; the shell corresponds with the outer or hard coating of the seed; the white and yolk of the egg appear as the albumen, or meal of the grain; while the embryo of the egg has its analogue in the germ of the grain. A remarkable change takes place during germination; the glutinous constituent has passed from the body of the grain to the *radicula*, or rootlet, which has grown to nearly the length of the grain, while about one-half of the starch has been converted into sugar. This conversion is the aim of the malting, as by this means the sugar can be readily dissolved. The grain is supposed to have been sufficiently treated when the plumule, or *acrospire*, has attained a length equal to two-thirds of the entire length of the grain. The operation of germination is the same with all kinds of grain employed in brewing. The conditions of success are—the saturation of the grain with moisture, and a temperature of not higher than 40° nor lower than 4°, with access of air and exclusion of light.

(*a*) *The Softening or Soaking of the Grain* is accomplished in large cisterns of wood, sandstone, or cement, half filled with water. The grain is poured into the water, and, after the lapse of an hour or so, sinks to the bottom of the tank, only the inferior and diseased seed remaining on the surface, to be removed with wooden shovels, and thrown aside for use as fodder for horses, cattle, &c. The steep water receives the soluble constituents of the husk of the seed, and becomes of a brown colour and peculiar flavour, with a decided inclination to lactic, butyric, and succinic acid fermentation. The duration of the softening varies according to the age of the grain, the temperature of the water, &c. A young, fresh grain requires forty-eight to seventy-two hours' soaking, while an older grain, containing more gluten, is not thoroughly softened under six to seven days. Grains of equal age and constitution must be soaked together, to obtain an equally softened product. After sufficient soaking, the grain

is allowed to drain for eight to ten hours, then taken out and thrown into heaps on the floor of the malt-house. The sufficiency of the soaking is ascertained—(1) By pressing the grain between the finger and thumb-nail, when, if sufficiently moistened, the germ, or embryo, will be projected. (2) The husk is easily destroyed by pressure between the fingers. (3) When crushed with a piece of wood the grain yields a floury mass. The grain when softened has a peculiar aroma, resembling that of apples. The quantity of water usually absorbed by the barley amounts to 40 to 50 per cent. of its weight, while the grain correspondingly increases in volume 18 to 24 per cent. During this absorption the grain loses 1·04 to 2 per cent. of its own weight in solid matter. Lermer states, that in fresh steep water he has found succinic acid in the proportion of 30 grammes to 1 bushel of grain soaked.

(*b*) *The Germination of Softened Grain.*—As soon as the grain is thoroughly saturated with moisture, the conversion of the starch into sugar commences. When germination has proceeded far enough it must be stopped, as about this time the formation of sugar has reached a maximum. The softened barley is, as before stated, transferred to the floor of the malting-room, where it is "couched," or placed in a layer of 4 to 5 inches in thickness. Here the germination proceeds till the plumules have attained the desired length. The temperature rises some 6° to 10° on account of the heat developed during germination, and consequently much of the moisture is dissipated. The chief art of the maltster consists in stopping the germination at that point when the plumules and roots commence to draw upon the constituents of the grain. The duration of the germination varies, during the warmer months of the year, from seven to ten days, while towards autumn the process will not be completed under ten to sixteen days, but the average duration is eight days. The grain, during germination, loses about 2 per cent. of its weight, probably by the oxidation of the carbon to carbonic acid by the oxygen of the air.

(*c*) *The Drying of the Germinated Grain.*—The grain is now removed to the drying floor (*Welkboden*), where it is exposed to the air in layers 3 to 5 centimetres in depth, and turned about with rakes six to seven times daily. When the malt becomes dry it is cleared from the rootlets, some of which drop off by themselves, while others have to be removed by winnowing. Malt must be dried for the making of most kinds of beer, and has to undergo a roasting process before quite fitted for use. This drying or roasting is effected in a malt kiln or cylinder heated by flues to the boiling-point of water. During the roasting the malt acquires a darker colour, due to the conversion of the remainder of the starch into sugar. The equality of the temperature is of the utmost importance, so that one part of the malt may not be more strongly heated than another. Before the malt is submitted to this operation, however, it is first heated to 30° or 40°. By this means some of the starch is converted into gluten, and forms a coating to the grain impervious to water, the malt being in this stage known as "bright" malt from its smooth, glossy appearance.

The malt kilns consist essentially of the drying plates upon which the malt is laid, and the heating flues. The plates used to be of stone or sheet-iron, but modern brewers employ wire-wove frames, placed one above the other, so that the hot air from the flues beneath may ascend through the interstices. The flues are generally of sheet-iron for the better conduction of heat to the surrounding atmosphere. Coke is used as fuel on account of the absence of smoke, as with coal or wood, in the event of a leakage in the flues, considerable damage would be done to the malt.

The malt is not all dried at the same heat (50° to 100° C.), but is distinguished as pale, amber, brown, or black malt, according to the degree of heat to which it has been exposed. Pale malt results from heating to 33° to 38°; amber, from a temperature of 49° to 52°; and brown from the rather high temperature of 65·5° to 76·5°. Black malt, commonly called patent malt, is prepared by roasting in cylinders, like

coffee cylinders, at a temperature of 163° to 220°. These darker malts are used in England for colouring porters and stouts.

100 parts of barley give 92 parts of air-dried malt. The loss of 8 parts may be thus accounted for :—

In the steep-water	1·5
During malting	3·0
During germination	3·0
Other losses	0·5
Total loss	8·0

The moisture in air-dried malt amounts to 12 to 15·2 per cent., and is expelled during the kiln drying. According to C. John (1869), 100 parts of dried barley give—

	I.		II.
Malt	83·09	...	85·88
Plumules	3·56	...	3·09
Radicules (rootlets)	4·99	...	4·65
Fermentary products	8·36	...	6·38
	100·00	...	100·00

The change undergone during the drying or roasting of the malt is shown in the following table, the result of Oudeman's analyses :—

	Air-dried Malt.		Kiln-dried Malt.		Strongly Dried Malt.
Products of roasting	0·0	...	7·8	...	14·0
Dextrine	8·0	...	6·6	...	10·2
Starch	58·1	...	58·6	...	47·6
Sugar	0·5	...	0·7	...	0·9
Cellulose	14·4	...	10·8	...	11·5
Albuminous matter	13·6	...	10·4	...	10·5
Fat	2·2	...	2·4	...	2·6
Ash	3·2	...	2·7	...	2·7

The amount of sugar is undoubtedly increased during the process ; and the dextrine appears to increase with decrease of starch, and *vice versâ*. The conversion of starch into dextrine and sugar is effected, as far as is known, by the agency of diastase. Dubrunfaut has (1868) shown that malt presents another substance similar in its effect to diastase, and which he termed *maltin*. This principle is found to be much more active than diastase, so that with the same quantity of maltin which a known quantity of malt contains, ten times as much beer can be obtained as when diastase only is employed. Dubrunfaut has also found a second but less active substance. Its behaviour with respect to the decomposition of starch is similar to that of diastase; malt contains 1½ per cent., while only 1 per cent. of maltin is found. The treatment with alcohol necessary to obtain diastase destroys the maltin. Dubrunfaut believes diastase to be only a less active modification of these new substances.

The author is of opinion that the building in which the process of germination is conducted may have its windows advantageously constructed of violet glass.

The combustion value of 1 kilo. of starch is = 4200 heat-units. For 100 kilos. of dry malt there will be evolved during the process of germination 6·7 × 4200 = 28,100 heat-units.

Pneumatic Malting.—In order to remove the carbon dioxide, which interferes with germination, and to prevent an excessive rise of temperature, so-called pneumatic malting has been devised. Galland, *e.g.*, in his pneumatic maltings keeps the air moist by means of a tower (Fig. 514), which contains coke resting on the gratings, *b* and *c*. The air, previously heated, enters through the pipe *a*, ascends to meet the descending water through the bed of coke, and passes through *C* into the recipients, *A* and *E*, which contain the barley. The requisite water is let into the cistern, *w*, through a

cock, *J*, flows through the overflow, *g*, to the sprinkling apparatus, *r*, and then downwards. In order to use the water over again, it is lifted by the pump, *H*, below the filter, *k*, through which it rises to the cistern, *w*. In the softening-beck, *A*, there is a perforated false bottom, *d*. The barley to be malted is softened in this beck for forty-eight to sixty hours in water. When the water is removed the grain soon begins to sprout. Contrary to the present process, it is left undisturbed for two or three days, the softening-beck being meantime kept closed with a plate. In order to remove the heat which is evolved, fresh air is conveyed to the barley through the pipe *B*, which escapes through the pipe *D*. The sprouted grain falls through the hopper, *t*, and the aperture, *o*, into the drum, *E* (Fig. 515). This consists of a sheet-iron cylinder, closed at both ends. The partition, *s*, is provided with openings, *d*, with which are connected the channels *e*, made of sieve-plate. The air entering at *I* arrives from the ante-chamber, *N*, in the channels *E*, traverses the barley, and is drawn off by the intermediate sieve-tube, and the main, *S*. The drum is continually turning on the rollers, *G*. The movement can be effected in various manners—*e.g.*, as in Fig. 515, by an endless screw, *V*, which plays into a circuit of cogs. During the first four days after introduction into the drum, *E*, fresh, moist air is continually supplied to the barley from the coke-tower through the pipe *P*. As soon as the germination is retarded, there is supplied for two days a suitable mixture of fresh, moist, and warm air, the latter coming from a hot-air chamber through an opening in the tubing, *P*. Then dry air at 50° is allowed to enter, and the temperature is gradually raised until the malt is ready.

Fig. 514.

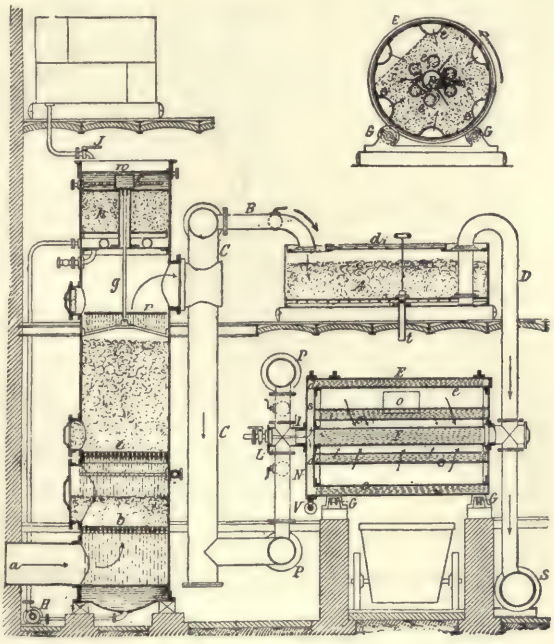
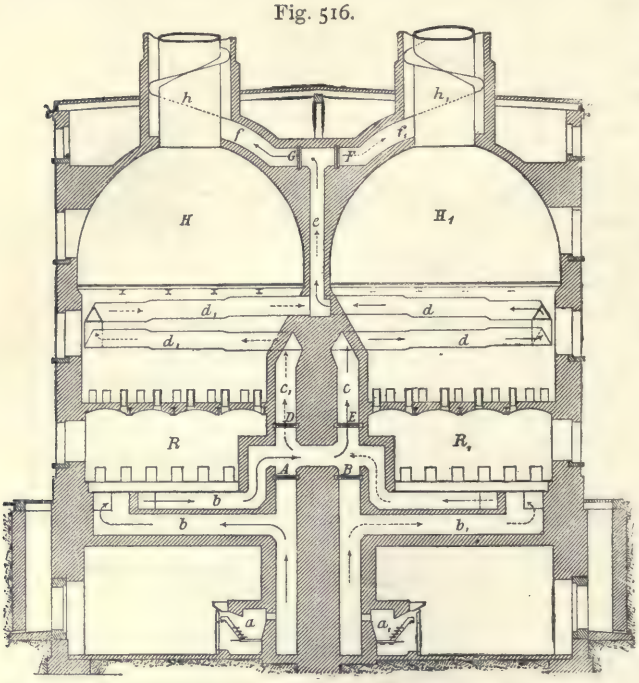


Fig. 515.

In Leicht's malt kiln (Fig. 516) the combustion gases pass from the fire *a*, through the flues *b*, beneath the preliminary air-heaters, to the flues *c*, in which case the movable dampers *A*, *B*, and *D* are closed, whilst *E* is open; from the flue *c*, the fire-gases pass through the iron flues *d*, to the common duct, *e*, and if the damper *F* is closed and *G* is open, through the flue *f*, to the vapour chimney *h*. Inversely, the combustion-gases from the fire a_1 take their way through the flues b_1, c_1, whilst the dampers *A*, *B*, and *E* are closed, and *D* is open, to d_1, *e*; and, further, if *G* is closed and *F* open, to b_1, and then to the vapour chimney h_1, in the direction indicated by the dotted arrows. By alternately opening and closing the dampers *A*, *D*, and *B*, *E*, the combustion-gases can be led from the fires, *a* or a_1, directly into the chimney above, whereby the roasting of the malt on each floor is assisted. Further, the escaping gases can be led either to *h* or h_1, by opening and shutting dampers *F* and *G*, in order to promote the draught in the required direction, according as the drying is conducted on *H* or H_1. In practice this is done alternately day by day, one flue being

used for drying and one for roasting. If H is used for drying, the fire a and the preliminary heating chamber are active, and the draught is accelerated by the heated chimney h, whereby the temperature on the floor H remains moderate even with the strongest fire, whilst the radiant heat is given off in the flues d for roasting on the floor H_1.

Fig. 516.



If the temperature on the floor H_1 is not sufficient for roasting, the fire a_1 is used in assistance, with the open dampers B and E, so that the fire gases may pass directly into the flues d.

In a trial-malting all the samples of barley are steeped, malted, and dried under identical conditions. The barley, freed as far as possible from stones, the seeds of weeds, oats, &c., is weighed, washed till the water runs off clean, and then steeped in a cylindrical glass with an equal weight of water. After some hours the floating grains are taken off, air-dried, and weighed. The steeping water is changed every twenty-four hours, at a maximum temperature of 15° in the room, and is replaced by an equal quantity of water. After the barley has reached the right degree of softness it is spread on a horse-hair sieve in a layer 6 to 8 centimetres in height. Each sieve is laid over a flat vessel containing water, and covered with a wet cloth. In these experimental maltings on the small scale it is necessary to free the barley from dust before steeping, rubbing the grains cautiously in water with the fingers or on a cloth, as otherwise mouldiness would set in. The malt is then weighed and spread on a small square drying-floor heated with gas, where it remains twenty-four hours. The drying takes twenty-four hours at a maximum temperature of 36°; the heat is gradually raised, and the malt is finally roasted at 80° for five hours.

Origin.	Dry Matter in Barley.	Average Weight of an Air-dried Grain.	Floating Grains of Air-dry Barley.	Time of Steeping.	Time of Germinating.	Germination began after	Green Malt from Air-dry Barley.	Roasted Malt, free from Germs, from Air-dried Barley.	Moisture in Roasted Malt.	Dry Malt Substance from Dry Barley Substance.
	p. c.	mgrm.	p. c.	hours.	days.	hours.	p. c.	p. c.	p. c.	p. c.
Hungary	85·87	37·64	0·73	75	11·00	41	148·1	83·2	5·79	91·27
Slavonia	87·03	38·02	0·44	92	9·40	34	153·1	84·4	6·55	90·62
Regensburg	84·65	41·17	1·28	79	8·90	47	157·3	81·0	4·80	91·09
Bohemia	86·31	44·50	0·82	74	8·90	38	151·9	83·3	5·40	91·30
Franconia	82·35	47·40	1·40	95	10·25	57	146·4	78·5	4·72	90·82
Saale	86·56	43·60	0·56	73	9·33	48	153·7	83·3	5·42	91·01
Moravia	86·70	38·65	1·34	94	9·25	46	158·2	80·8	5·07	89·17
Sweden	81·69	39·93	1·14	92	11·05	92	152·9	79·6	4·85	92·86

The nitrogen of the barleys and the malts obtained, with the constituents of the ash, amounted to—

	Barleys.							
	1.	2.	3.	4.	5.	6.	7.	8.
N	1·809	1·629	1·877	1·809	1·859	1·696	1·750	1·605
Ash	2·690	2·640	2·850	2·570	2·810	2·860	2·650	2·630
SiO_2	0·599	0·671	0·656	0·651	0·826	0·579	0·645	0·711
P_2O_5	1·010	0·790	1·078	0·923	0·798	0·817	0·804	0·767
SO_3	—	—	—	0·082	0·147	—	—	0·107
CaO	0·056	0·059	0·065	0·062	0·059	0·037	0·640	0·067
MgO	—	—	—	0·231	0·229	0·216	—	0·224
Fe_2O_3	0·009	0·013	0·016	0·015	0·007	0·013	0·009	0·003
K_2O	—	—	—	0·315	0·608	0·528	—	0·592
	Malts.							
N	1·625	1·600	1·857	1·798	1·729	1·568	1·733	1·413
Ash	2·480	2·390	2·440	2·300	2·420	2·350	2·320	2·310
SiO_2	0·598	0·711	0·677	0·644	0·725	0·556	0·770	0·651
P_2O_5	0·929	0·868	0·904	0·708	0·779	0·784	0·830	0·693
SO_3	0·029	0·054	0·012	0·029	0·012	0·019	0·031	0·058
CaO	0·091	0·072	0·087	0·077	0·084	0·096	0·085	0·082
MgO	0·253	0·266	0·236	0·219	0·239	0·239	0·219	0·212
Fe_2O_3	0·022	0·018	0·019	0·014	0·017	0·011	0·015	0·015
K_2O	0·468	0·363	0·470	0·367	0·385	0·417	—	0·407

It is seen how different is the loss in the several constituents of barley on malting. One part of the loss is due to the steeping water, which has a lixiviating action. Another part consists of the matters removed in the germs. Though the Munich water used in the experiments was not very hard, it did not extract any lime, but yielded some to the grain.

Balke examined several specimens of barley of the season 1883, and of the malts obtained from them. He obtained in percentages—

Origin.	Barley.	Dry Substance.				Germ-power.
	Dry Substance.	Starch Value.	Proteine N×6·25.	Ash.	P_2O_5 in Ash.	
					Per cent.	Per cent.
Moravia, I.	84·84	64·8	8·89	2·77	31·82	98·0
Moravia, II.	85·82	69·2	9·68	2·76	35·14	95·0
Silesia	85·19	63·2	10·71	3·02	20·54	84·0
Magdeburg	84·77	68·9	10·77	2·56	37·19	96·0
Stumsdorff	87·75	71·4	10·07	3·08	28·75	95·8
Coethen	84·84	69·9	10·16	2·58	37·80	97·5

Origin.	Malt.	Dry Substance.				Extract.	
	Dry Substance.	Extract.	Proteine N×6·25.	Ash.	P_2O_5 in Ash.	Maltose.	Maltose : Non-maltose = 1.
						Per cent.	
Moravia, I.	91·18	75·54	11·79	2·65	38·50	69·50	0·46
Moravia, II.	92·22	73·68	9·40	2·85	32·18	72·30	0·39
Silesia	89·35	75·26	8·53	2·48	37·35	68·72	0·45
Magdeburg	89·34	72·90	10·44	2·39	40·00	72·71	0·38
Stumsdorff	93·30	76·19	10·25	2·39	—	70·23	0·31
Coethen	93·20	74·93	9·94	2·49	—	70·63	0·31

The proportion of soluble nitrogenous constituents of different malts in percentages of the dry matter amounted, according to Salamon (1886), to—

Origin.	Total Nitrogen.	Albuminoid Nitrogen.	Peptonic Nitrogen.	Amidic Nitrogen.	Unknown Nitrogen.
England, good	0·6148	0·1200	0·0340	0·4090	0·05490
England, ordinary	0·6167	0·1441	0·0074	0·3804	0·08490
Scotland	0·5404	0·0514	0·0149	0·4025	0·07160
France	0·7147	1·0470	0·0624	0·5000	0·07476
Denmark	0·7111	0·1393	0·0634	0·5084	
Moravia	0·6159	0·1435	0·0438	0·4286	

Or in percentages of total nitrogen—

England, I.	19·51	5·53	66·02	8·94
England, II.	23·36	1·20	61·68	13·76
Scotland	9·51	2·75	76·33	11·41
France	14·64	8·73	69·95	6·68
Denmark	19·59	8·91	71·50	
Moravia	23·30	7·11	69·59	

According to Lintner and Aubry, good malt should yield an extract of at least 71 per cent. of its dry substance. In the extract there should be 64 to 69 per cent. maltose, and hence the proportion of maltose to non-maltose in the extract should be as 1 : 0·45 to 1 : 0·55. If the proportion is higher, say 1 : 0·30, the beers ferment too strongly and bear little head; if it is lower, as 1 : 0·60, there is too little maltose in the wort, and the fermentation is feeble. These proportions are doubtless correct for the full-bodied Bavarian beers, but in malts for the light and vinous North German beers the most favourable proportions of maltose to non-maltose in the extract are 1 : 0·35 to 1 : 0·47, the maltose in the extract being 68–75 per cent. Practice shows that such malts yield normal worts, fine fermentations, and beers of a good flavour. A further character which Lintner and Aubry demand in a good malt has been fully confirmed—*i.e.*, a good malt should be completely saccharified in twenty minutes, if mashed at 70°.

The object of the malting process is to form a non-organised ferment, *diastase*, at the expense of the nitrogenous constituents of the barley. This starch, in the subsequent mashing process, splits up the starch into maltose and dextrine. According to Zulkowsky (1878), the mean composition of a purified diastase obtained from barley malt is—

Carbon	45·57
Hydrogen	6·49
Nitrogen	5·14
Ash	3·16
Oxygen and sulphur	37·64

A second non-organised ferment, generated during the malting process, is *peptase*, which during mashing converts the protein compounds into peptones and para-peptones. A part of the constituents of the gluten, the parenchyma in which the starch granules are embedded, is rendered soluble or much loosened. The starch is so modified that it is turned into paste at a lower temperature.

The Production of the Wort.—In Bavaria, the *Schenk*, or *pot* beer, is brewed in the winter, and the *Lager*, or *store* beer, in the summer. The winter beer is brewed during October to April, when the highest range of the thermometer is 12° to 13°. A part of the beer by a short storing is set aside for winter consumption, while the remainder is used during the summer months.

1 volume of malt gives on an average 2·5 to 2·6 volumes of winter beer.
1 „ „ „ 2·0 to 2·1 „ summer beer.

2. *Preparation of the Wort.*—Under this head is included the preparation from

malt of the wort—a saccharine fluid containing dextrine—and the flavouring with hops. The general method of preparation is in three operations—

a. The bruising of the malt.

b. The mashing.

c. The boiling and flavouring of the wort with hops.

a. The Bruising of the Malt.—Beer-wort, or the wort, as it is generally termed, is obtained by means of the extraction of the bruised malt with water. To the end that all the active principles may be extracted from the malt, it must be bruised or ground to a fine meal. The obtaining of a clear liquor, after the extraction, is effected by means of filtration. The grinding is ordinarily performed in a malt mill, a machine with rollers being preferred, as affording a more equable product.

b. Mashing.—The mashing is a most important operation, on success in which depend many of the good qualities of the beer. It is during this operation that not only are the sugar and dextrine already existing in the malt set free, but the unconverted starch, by the aid of diastase, water, and a favourable temperature, suffers conversion into sugar and dextrine. Lermer found, in the best cases of mashing, that only half the starch was converted into a corresponding quantity of sugar. The operation is very variously performed, but generally may be considered as effected by either of two methods :—

(1) *The Decoction Method.*—After the infusion has been made the mash is brought to the boiling-point, and

(α) A portion of the water evaporated to form a thick mass (*thick mash boiling*). At a subsequent stage, only a portion of the mash having been thus treated, the remainder of the mash is added; and

(β) The whole of the mash is heated to the boiling-point (*clear mash boiling*). The hops are added during the clear mash boiling.

(2) *The Infusion Method*, according to which the mash is prepared at a certain degree of heat, but never attains the boiling-point. The crushed malt is thrown into hot water (*first cast*) in the mash tun, and when the mash has reached a certain saccharine condition, a further addition of water is made (*second and third cast*). The infusion method is much employed in North Germany, France, England, Austria, and Bavaria.

The mashing vessels are either round tubs or wooden cisterns with a double bottom, the upper being perforated, and about an inch above the true bottom. Between the bottoms is a tap through which the wort is drawn off. In large breweries these bottoms are of metal instead of wood. The hot water is supplied from the bottom and not from the top of the vessel. Under the mashing vessel is situated a large reservoir, either of stone, cement, wood, or masonry, and destined to receive the fluid run off from the mash. The continuous stirring of the contents of the mash-tun or tub is effected either by hand or machinery driven by water or steam power.

(1) *Decoction Method.*—The general description of the mashing process having been given, we now pass on to the particular method of preparing the wort by decoction. The infusion takes place in the mash-tun, in which the required quantity of water is placed, and the malt to be mashed shaken in. The quantity of water employed in making the infusion is generally in the proportion of 202 volumes of water to 100 volumes of malt, both at the ordinary temperature. After the bruised malt has been well stirred in the water, the whole is allowed to stand for six to eight hours. During this time the necessary quantity of water is heated to the boiling-point in the copper. The quantity of water used to prepare an estimated quantity of beer is termed the

"cast," and the quantity of malt the "yield." In Bavaria the quantity of beer prepared from a defined quantity of malt is as follows:—

100 volumes of malt yield { 202·3 volumes of Schenk beer.
173·0 „ „ Lager beer.

In order to produce this quantity of beer an equivalent quantity of water must of course be employed, so that, in a Bavarian brewery, to 100 volumes of malt there are taken of water—

	Schenk Beer.		Lager Beer.
For infusion . . .	202·3 vols.	...	202·3 vols.
For mashing . . .	170·0 „	...	130·0 „
	372·3 „	...	332·3 „

These proportions vary according to the quality of the grain, the state of the weather, the length of time of keeping, &c.

The various modifications of the decoction method are—(*a*) The Bavarian or Munich method; (*β*) The Augsburg-Nuremberg, or Swabian method, sometimes termed "sediment brewing" (*Satz brauen*).

(*a*) *Thick Mash Boiling.*—According to the Munich method (thick mash boiling) the cast of water is divided into three portions, two of which are poured into the mash-tun to form a paste with the bruised malt. After this mash has stood for two to four hours, the remaining third of the water, which during this time has been heated to the boiling-point in the copper, is added, the whole of the mash attaining thereby a temperature of 30° to 40°. Then follows the first thick mash boiling; for this purpose the brewer draws the mashed grain to one side of the tun, and removes a portion to the copper, where for schenk beer it is boiled for thirty minutes, and for summer beer for seventy-five minutes. The quantity of mash boiled at each operation is generally about half the cast. The boiling mass is returned to the mash-tun. Then follows the *second* thick mash boiling, which for schenk beer lasts seventy-five minutes, and for summer beer an hour. By means of the first boiled mash the contents of the mash-tun are raised to a temperature of 48° to 50°, and by the second addition to 60° to 62°. After the finishing of the second mashing the *clear mashing* begins; that is, the thinly fluid part of the mash is placed in the copper and boiled for about fifteen minutes, and is then returned to the mash-tun. The temperature of the mash is now 72° to 75°, and is most suited for the formation of sugar. The mash remains in the covered tun 1½ to 2 hours. During this time, and as soon as the clear mash has been removed from the copper, the latter is refilled with a sufficient quantity of water for the purposes of brewing small beer. When the sugar has been properly formed and dissolved in the wort, the latter is removed from the mash-tun to the fermenting vessels. The remaining mash is then treated with hot water to yield small beer, 1 bushel of malt yielding 35 to 50 quarts of this beer. The residue of the small beer is again treated with water, the resulting infusion being employed in vinegar making. The residue from this process is used as fodder for cattle.

The thick mash boiling is by no means a rational method, as the separation of the mash and the several removals are unnecessary labour, and do not contribute so much to the complete extraction of the malt as is generally supposed; the high temperature renders a portion of the diastase ineffective, while much of the starch remains unconverted into dextrine and dextrose.

All who have tried to reduce the brewing process to simple methods based upon sound chemical and physical principles declaim against the process of thick mash boiling, stating—and with good reason, proved by experiments—that the advantages of this method are absurdly overrated; and that, in order to lessen the bad effects of this method as much as possible, it should be replaced by a method of hot mashing—viz., at a temperature of from 60° to 65°.

(β) *Augsbury Method.*—Distinct from the foregoing mash methods is the so-called "sediment brewing" used in many Swabian and Franconian breweries. It essentially consists in treating the bruised malt with cold and then with hot water, to obtain a saccharine wort. The bruised malt is mixed with cold water in the mash-tun in the proportion of 7 Bavarian bushels to 30 to 35 eimers (each = 68·41 litres) of water. After standing for four hours, two-thirds of the fluid is drawn off. During this time a quantity of water (48 eimers to 7 bushels of bruised malt) is brought to the boiling-point in the copper; a portion of this water is now added to the contents of the mash-tun, which thus attains a temperature of 50° to 52°, while the liquor or weak wort drawn off from the mash-tun is poured along with the rest of the water in the copper. The liquor that has been drawn off contains albumen, diastase, dextrine, and dextrose. The mash is allowed to stand for a quarter of an hour in the tun, when the fluid is entirely drawn off, transferred to the copper, and heated to the boiling-point. This is termed the "first mash." While this is going on, enough fluid will have drained from the malt in the mash-tun to fill the space between the double bottoms of the tun; this fluid is at once removed to the cooling vessels. The fluid heated in the copper is now returned to the mash-tun, the entire contents of which attain a temperature of 72° to 75°. This "second mash" is, after an hour's interval, followed by a "third mash." The wort is then run into the cooling vessels.

(2) *Infusion Method.*—The infusion method is distinguished from the decoction method by a slight difference in the procedure, the bruised malt being treated with water at a temperature of 70° to 75°, but without any portion of the mash being boiled. The method is that usually employed in this country, North America, France, Belgium, and North Germany.

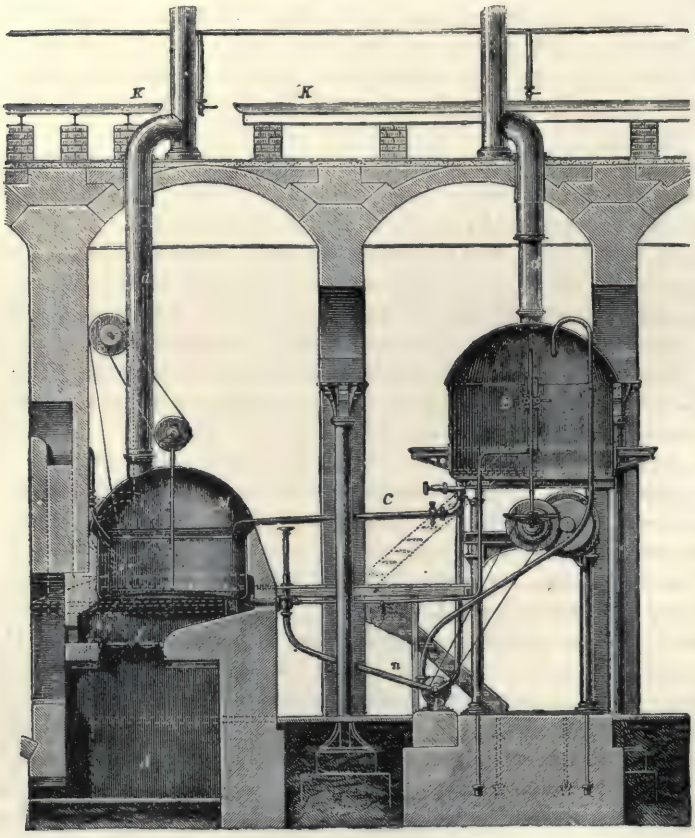
The water intended to be used for the mashing process is, according to the initial temperature of the water the brewer has at hand, heated, either wholly or in part, in the copper, the temperature being raised in winter to 75°, in summer to from 50° to 60°. The necessary quantity is first poured into the mash-tun, the bruised malt being next added, and the mixture made up so as to form a moderately thin paste. Water is heated to the boiling-point in the copper in order to proceed further with the mashing process. As soon as a sufficient quantity of water boils it is—usually by means of properly constructed pipes—allowed to run into the mash-tun, wherein it is considerably cooled owing to the colder liquor present in that vessel; the increase of temperature of the contents of the tun to 75° (the most suitable for saccharification) is gradually made in order to prevent the formation of starch paste, whereby the formation of diastase would be interfered with. Since the conversion of amylum (starch) into dextrine and dextrose proceeds gradually only, it is clear that the contents of the mash-tun should be kept at the temperature suitable for that process; while, however, on the other hand, care has to be taken to prevent the mash becoming sour by the formation of lactic (probably also propionic) acid.

The progress of the formation of dextrine and dextrose is best ascertained by the help of an aqueous solution of iodine, or preferably of iodine dissolved in iodide of potassium, in the proportion of 1·0 gramme of iodine and 1·0 of iodide of potassium to 100 c.c. of water; this solution will at first give with a sample of the mash a dark blue coloration, next a wine red, and finally, when only dextrine and dextrose are present, no coloration at all. The addition of 2 or 3 drops of the clear wort to a small quantity of this iodine solution is sufficient for testing. When the mash has been kept for about one hour's time at the temperature most suitable for the saccharification, the wort is run either into a large reservoir, or into a vessel kept expressly for this purpose, or, lastly, at once into the copper; a fresh quantity of water is then poured into the tun, and the contents of the tun are allowed to remain for half to one hour at a temperature of 75°. It is of course quite evident that the infusion

method may be varied as regards the quantity of water and repeated number of infusions; but in order to brew a beer of a certain and fixed brand it is requisite that the degree of concentration of the wort be always the same. For the purpose of ascertaining the degree of concentration, Balling's saccharometer is generally employed, which instrument, when put into sugar solutions, indicates the percentage of sugar they contain. Balling has shown that solutions of dry extract of malt have the same specific weight as cane-sugar solutions of equal percentage. For use in a brewery the saccharometer need only be graduated for solutions varying between 20 and 30 per cent.

Extractives of the Wort.—The quantity of extract which a wort should contain depends, of course, upon the quality of the beer which the brewer desires to make, and differs according to the nature of the beer, whether it shall be thick, heavy (rich in extract), or strong (of great alcoholic strength). The quantity of malt extract varies in different beers from 4 to 15 per cent., that of the alcohol from 2 to 8 per cent. 1 per cent. of sugar in the wort yields after fermentation 0·5 per cent. of alcohol. To produce a beer containing 5 per cent. of alcohol and 7 per cent. of malt extract, the wort should, before fermentation, mark the degree on the saccharometer corresponding to 17 per cent. A beer of 3·5 per cent. of alcohol and 5·5 per cent. of malt extract will result from a wort containing 12·5 per cent. of sugar.

Fig. 517.

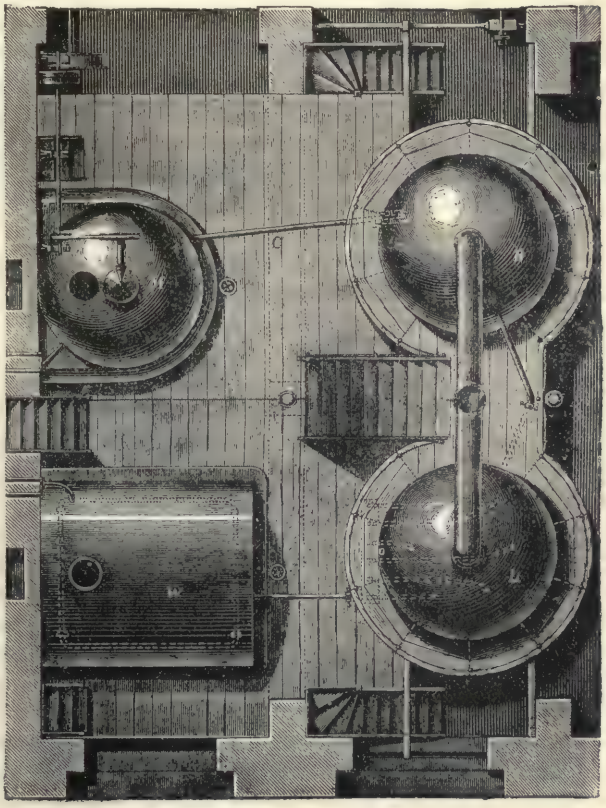


c. Boiling the Wort.—The prepared but not yet boiled wort contains dextrose, dextrine, some unconverted starch, protein substances, extractive matter, and organic salts. The colour of the wort is a brown or yellow-brown, according to the variation of colour of the malt from which it has been obtained. The odour is agreeable and the taste sweet. The wort exhibits an acid reaction to test-paper, owing to the presence in that fluid of small quantities of free phosphoric, lactic, and probably other acids; but in case the wort has by accident become sour, or if wort is made purposely from already exhausted grain which has become sour, this reaction is far stronger, and may be ascertained by the odour, owing to the formation of volatile acids, among which butyric, and in the latter case lactic and propionic acids,

are present in large quantity. The boiling of the wort aims at its concentration, and also at the extraction of the bitter principle of the hops; further, also, for the purpose of coagulating and precipitating a portion of the albuminous substances by the aid of the tannic acid contained in the hops. This latter reaction renders the wort clear. In many breweries gypsum is added to the boiling wort to reduce the whole of the nitrogenous substances. The boiling is generally effected in copper cauldrons (technically, also simply, "the copper"), set in masonry over a fire-grate. The fire is very carefully disposed, to prevent the burning of the wort, as the pans are exposed to the direct action of the flame. The manner of hopping (as it is termed)—that is to say, the mode of adding the hops to the wort—varies in different breweries, and depends, as regards quantity, also upon the quality (strength) of the hops, the larger or smaller amount of extract contained or desired to be retained in the beer, and last, but not least, the mode of preservation and length of time it is intended to keep the beer.

Figs. 517 and 518 show the ground plan and section of the mashing-house in the Bavarian State Brewery in Weihenstephan. The bruised malt is mixed with water in the beck, *B*, which is fitted with an agitator. A part of the mixture is allowed to flow down, through the pipe *C*, into the pan, *M*. Here it is boiled with agitation; the hot mass flowing off is then brought back through the tube, *n*, by means of the centrifugal pump, *P*, into *B*; it is well mixed, another portion boiled in the pan, *M*, so that, when it has been pumped back into *B*, the temperature desired for converting the starch into maltose and dextrine (68° to 70°) is reached. When the formation of sugar is completed the mixture is brought into the clearing tank, *L*, provided with a perforated false bottom, in which the grain remains whilst the wort flows through the tubes, *o*, into a common channel, and thence to the wort-pan, *W*, in which a steam pan is laid. Here it is boiled up with hops. The watery vapours escape through the pipes *a*. The wort flows through a strainer, and is pumped into the cooling-becks, *K*.

Fig 518.

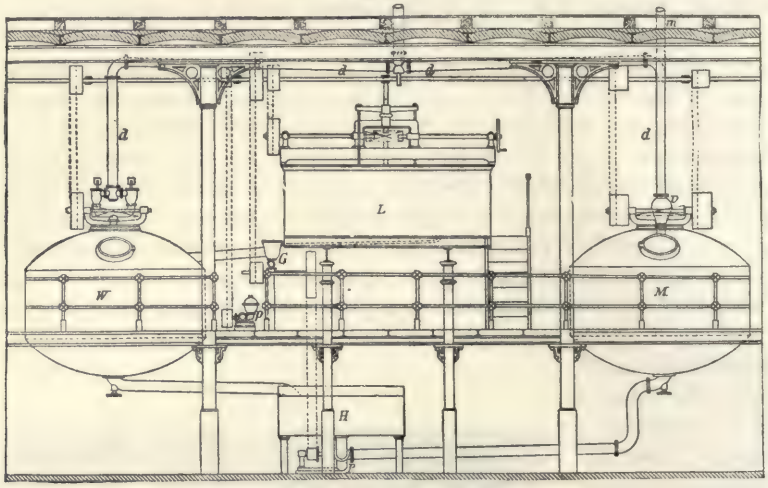


Lintner prefers the Bavarian to every other method of decoction, with two thick mashes and a clearing mash.

A pan-mashing adopted in the brewery at Nürtingen, with steam washing, deserves more general attention. The mashing-pan, *M* (Fig. 519), is fitted in the ordinary

manner with a thermometer, safety-valve, pressure-gauge, inlets for cold and hot water, double globular bottom, and cocks for the admission of steam. The preparatory mashing apparatus, *v*, is connected by the pipe, *m*, with the chest for bruised malt. A mashing machine with a double movement effects the regulation of the tem-

Fig. 519.



perature. The waste steam escapes through *d* to a preliminary water heater. The mash and clearing beck, *L*, contains a combined machine for stirring up and throwing out the grains, and is connected with the wort-pump, *p*. The wort-pan, *W*, is arranged like the mashing-pan, and in its jacket there is a glass introduced to show the level of the wort. All the vessels are made of sheet-iron, jacketed, and with double bottoms. The hop-pan, *H*, is connected with the circular pump, *P*.

Adding the Hops.—To make winter beer, which in Germany, as a rule, is consumed in four to six weeks after brewing, old hops (viz., one year old) are added in the proportion of 2 to 3 lbs. to a Bavarian bushel of malt (2·22 hectolitres). For summer beer, to be consumed in May and June, 4 to 5 lbs. of new hops are added to the bushel of dried malt; while for the beer for September and October consumption, 6 to 7 lbs. of new hops are employed with each bushel of malt. Among the constituents of hops which are active in the process of brewing, we may mention in the first place the bitter ingredient it contains (not correctly known, notwithstanding recent research), and which imparts to beer its bitter taste and narcotic property; further, the tannic acid, which combines, during the boiling of the wort, with a portion of such of its protein compounds as are not rendered insoluble by the boiling alone, and form together a precipitate, rendering the wort—previously turbid—quite clear, and also regulating the first and second (so-called after-) fermentation. The essential oil and resin met with in hops act to a certain extent as retarding the fermentation, and thus prevent the wort becoming converted into a sour liquid. The inorganic constituents of hops do not appear—at least cannot be directly proved—to be of much consequence. As regards the degree of concentration to be given to the wort by the process of boiling, it should be observed that the degree of concentration as ascertainable by the saccharometer should remain from 0·5 to 1 saccharometrical percentage under the degree of concentration which the wort should indicate at the beginning of the fermentation, because, while cooling, the wort gains in concentration just the percentage alluded to. The separation of the coagulated albumen does not take place until the temperature of the wort has reached 90°; and the quantity separated is greater from wort prepared by the infusion method than from that

prepared by the decoction method. As soon as, in a sample of the boiling wort taken from the pan and poured into a large test-glass, the suspended flocculent matter settles rapidly to the bottom of the glass, the boiling can be discontinued, the wort being then ready; but, in the infusion method, the boiling is continued for the purpose of further concentrating the liquor, and for this purpose it may even last for from five to eight hours. If the boiling only aims at the coagulation of the albuminous compounds, one hour in winter, and three-quarters of an hour in summer, is quite sufficient. As regards the hops, it is best to add them in a somewhat cut-up state, and not before the greater part of the albuminous compounds have been, as far as possible, precipitated by a good boiling of the wort. In order to extract the hops, the wort is either passed through a basket or through any suitably constructed perforated vessel retaining the hops, this vessel being placed in communication with the coolers; or the hops are boiled along with the wort; or, again, several portions of the wort are boiled successively along with the same quantity of wort; and lastly, even with the weakest wort or after-run.

Cooling the Wort.—The cooling of the wort to the degree necessary for the commencement of the fermentation is effected in large wooden, stone, or iron cisterns. As at a temperature of 25° to 30° C. the wort has a great tendency to set up lactic-acid fermentation, the cooling has to be very rapid in order that the temperature of the liquid may be soon much below 25° to 30°, and thus any danger of souring prevented.

The cooling of the wort is an operation which is performed in well-constructed buildings well ventilated in all directions and protected from rain, in which buildings the coolers are placed. Owing to improvements in the modes of cooling, it is now possible even to brew beer in localities (as, for instance, Montpellier and Marseilles, Barcelona and Naples) where formerly, on account of the prevailing high temperature during the greater portion of the year, brewing could not take place at all; while also, for the same reason, in various countries (America, United States, especially) excellent lager beer is brewed. The cooling vessels are generally only 6 to 8 inches deep, of wood, iron, or copper, and are placed in an airy situation near or immediately under the roof of the brewery. Metallic vessels are of course more effectual in cooling the wort in a short time than wooden ones; they are also more cleanly, and less liable to get out of order. In some breweries where a constant stream of cold water is available, the coolers are placed therein; but this is of course a matter entirely depending on the locality of the brewery. Without doubt the surest means of cooling the wort rapidly is by employing ice, either in blocks in the wort or in pans placed in the cooling-tuns. But, for economic reasons, this plan is not generally available. The temperature to which the wort is to be cooled is that best suited to fermentation, the next process to which the wort is subjected. The following are the temperatures at which fermentation most readily sets in, depending upon the temperature of the locality and upon the kind of fermentation :—

Temperature of the Locality where the Fermentation takes place.	Temperature of the Wort.	
	In Sedimentary Fermentation.	In Superficial Fermentation.
6° to 7°	12°	15°
7 „ 8	11	14
8 „ 9	10	13
9 „ 10	9	12
10 „ 12	7° to 8°	12° to 11°

The concentration of the boiled and hopped wort is expressed in degrees per cent. of the saccharometer.

The old cooling process has the defect that the wort is exposed for a long time to impure air, so that the benefit of pure air is rendered doubtful. In order to prevent the contamination of the wort with schizomycetes during cooling, the improved cooler (Figs. 520 and 521) has been used with success at the Carlsberg Brewery. The boiling vat runs through the pipe, *M*, into a large cistern of galvanised iron capable of holding 100 hectolitres. It has a roof-shaped cover, *B*, which can be raised and lowered, and closes the cistern by means of a water-joint. Through an opening in the middle of the cover there moves the axle of a screw, *D*; there are at the side of the cover two openings for the escape of steam, *E*, *F*, in which there are short tubes filled with cotton. There is also in the cover a tube, *G*, through which sterilised air can be introduced into the space about the wort, when the latter, after cooling, is allowed to stream down into the fermenting cellar, thus preventing the entrance of impure air. Into the lowest part of the cistern underneath the screw there opens a tube, *H*, with numerous small apertures; through these sterilised air is introduced, ascending through the wort in bubbles, and supplying it with oxygen. In the middle of the cistern lies a system of cylindrical tubes through which flows cold water to cool the wort. In the bottom there is an outflow for the wort, *N*, another, *O*, for droppings, and a third, *P*, for the deposited sediment and for the water required for rinsing and cleansing the apparatus. Lastly, there is a thermometer which shows the temperature of the wort in a man-hole, *R*. The air which is pumped into the cistern and rises through the wort has been previously freed from all organisms and germs by means of a cotton filter, and is consequently sterile. As soon as the wort has risen above the entrance places of the air, its access is permitted, and the wort remains in continual contact with the air until it is cooled down to a suitable temperature, or, in summer, so far that the cooling can be completed by means of ice. The stay of the wort in the apparatus does not require more time than its exposure in the cooling-becks. When all the wort is run into the cistern the water is allowed to flow through the cooling-worm, and the screw is set in action until the required temperature has been reached. The wort is left to stand quietly until the sediment has been deposited, and it can be conveyed into the fermenting cellar.

Fig. 520.

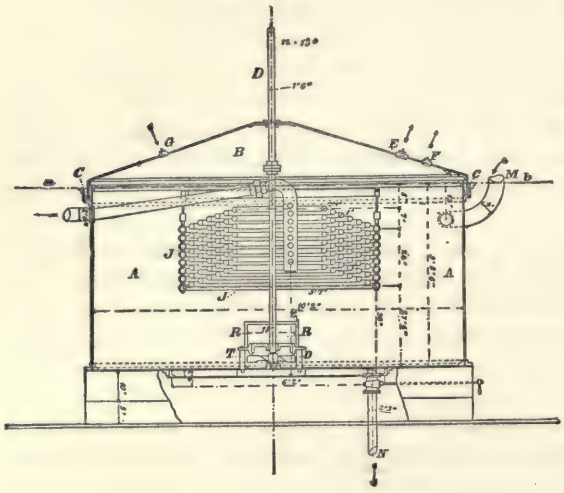
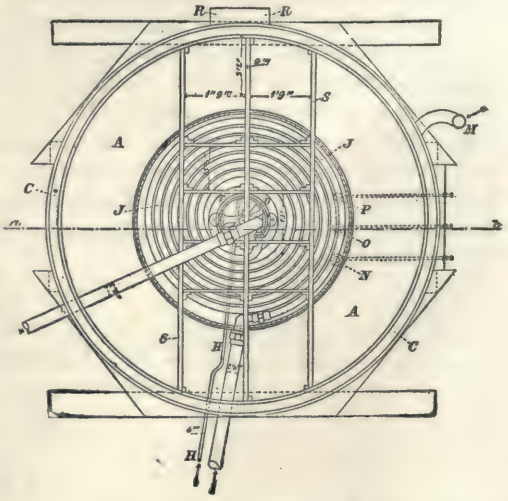


Fig. 521.



By means of two apparatus and mashings, each of 100 hectolitres, wort was cooled down daily at Alt-Carlsberg.

The point to which the wort must be cooled depends on the temperature of the cellar and the kind of fermentation. The following temperatures have been found most satisfactory in practice :—

Temperature of Cellar.	Temperature of Wort.	
	Bottom Fermentation.	Top Fermentation.
6° to 7°	12°	15°
8 „ 9	10	13
10 „ 12	7° to 8°	11° to 12°

According to J. Gschwändler's researches (1868), the under-mentioned Bavarian beer-worts had the following composition :—

Beer-wort.	Decoction.	Bock.	Sedimentary Method.	Infusion.
Sugar	4·850	7·100	4·370	5·260
Dextrine	6·240	8·600	7·610	6·680
Nitrogenous substances	0·790	1·350		
Other constituents	0·410	0·630	0·950	0·700
Specific weight	1·050	1·073	1·052	1·051
Extract (direct estimation)	11·870	17·050	11·980	11·940
„ (according to Balling)	12·290	17·680	12·930	12·640

While the wort remains in the cooler a yellow-grey or brown sediment is deposited, consisting of a compound of coagulated albumen with the tannic acid of the hops, and some starch similarly combined. This sediment, during the first cooling, is formed in quantities varying from 3 to 4 per cent. of the quantity of the cooled wort; the sediment, when washed and dried, amounts to 0·5 per cent. of the quantity of malt employed.

3. *The Fermentation of the Beer-wort.*—The wort, when cool, is run into the fermenting tanks, where fermentation sets in either spontaneously or is induced by the addition of yeast. The first kind—spontaneous fermentation—begins as soon as the wort, having been cooled down to the temperature most suitable for fermentation, is left to itself, and this fermentation is induced by the sporules of yeast (ferment cells) always present in all fermenting localities, which, meeting with the wort, find in that liquid the proper conditions for their growth. This kind of spontaneous fermentation is applied usefully in the brewing of the Belgian beers known as Faro and Lambick, which are rich in lactic acid. Usually, however, yeast is added to the wort, and there is avoided the dangerous first stage of spontaneous fermentation, for by the addition of the yeast a regular and rapid fermentation is set up, but yet so regulated that the yeast only gradually converts the dextrose into alcohol and carbonic acid.

The results of the researches made by Von Lermer and Liebig (1870) are of great importance for a rational basis of the brewer's business. According to these *savants*, an addition of sugar to a solution of dextrine, to which previously beer-yeast has been added, causes a large quantity of the dextrine to be converted into alcohol and carbonic acid, just as if the dextrine were sugar.

The higher the temperature of the wort and of the locality, the smaller the quantity of yeast required. A yeast formed by a violent fermentation and at a high temperature has more active qualities than yeast formed at a lower temperature and by a longer fermentation. The first spreads itself rapidly over the surface of the fluid, and is termed *superficial* yeast (*Oberhefe*); while the second sinks to the bottom of the vessel, and there continues its action; this is termed *sedimentary* or *bottom* yeast (*Unterhefe*).

The fermentations resulting from these two yeasts are respectively termed superficial fermentation (*Obergährung*) and sedimentary fermentation (*Untergährung*). The latter fermentation is induced in worts that are intended to yield beers of great durability, such as the Bavarian beers. The superficial fermentation is induced in such beers as are intended to be soon drunk. Where fermentation is induced in a wort at a low temperature and with deposit only (bottom-yeast), the so-called surface fermentation—that is to say, a vinous fermentation whereby yeast is carried to the surface of the fermenting fluid—is employed chiefly for such kinds of worts as are intended to produce a beer which is not required to be kept for any length of time, but rapidly consumed after having been brewed. The wort is in this instance generally rich in sugar (glucose); and while only a portion of this sugar is converted into alcohol (sweet beer being formed), the formation of a small quantity of alcohol (the wort being only lightly hopped) contributes largely to the preservation of this kind of beer. Surface fermentation is also induced in such kinds of worts as are either very concentrated or contain substances which to some extent retard, or might even altogether impede, fermentation; as, for instance, the empyreumatic substances present in a very highly roasted malt or a large quantity of hops, these conditions obtaining in the brewing of porter, stout, and, as regards hops, of bitter ale. Worts of this description come comparatively very difficultly into fermentation. Fermentation, no matter whether surface or sedimentary (the yeast is in this case slowly deposited as a sediment on the bottom of the vessel), exhibits the three following phases—viz.:

1. The chief fermentation, beginning soon after the addition of the yeast, characterised by the decomposition of the glucose, by the formation of new yeast, and by an increase of temperature.

2. The after-fermentation, during which decomposition of glucose continues slowly, while the formation of new yeast cells does not ensue so energetically as in the first phase, the suspended particles of yeast settling down, and the beer becoming clear.

3. The quiet or imperceptible fermentation, taking place when the after-fermentation is finished, is characterised by a further decomposition of glucose, while the formation of yeast is not perceptible to any extent.

Sedimentary Fermentation.—Sedimentary fermentation is employed in the brewing of the Bavarian schenk and lager beers, taking place in large fermentation vats containing 1000 to 2000 litres of wort. Recently, upon the suggestion of G. Sedlmayr, these vessels have been constructed of glass. The addition of yeast may be effected in two different ways: yeast may be either added to the wort, or a small portion of the wort is first separately brought into a state of fermentation, and next added to the bulk of the liquid. In the first case—*dry yeasting*, as it is termed—the yeast is placed in a small tub and wort poured over it, and, these substances having been well mixed, the whole of the contents of the vessel are thrown into the fermentation vats, and there worked about by the aid of a stirring pole. According to the second method—*wet yeasting* or *yeast carrying*—6 to 8 maas* of yeast are added to 100 maas of wort, and well mixed with about 3 eimers of wort, the mixture being allowed to stand for four to five hours. After fermentation has set in, the fermenting liquid is mixed with the wort in the fermentation tank. The yeast intended to be used for this purpose should be obtained from a former and normal fermentation; it should not be too old, should possess a pure odour (not be foul) and a thick consistency, and be frothy.

After the wort has been mixed with the yeast the following phenomena are exhibited:—After ten to twelve hours the decomposition of the dextrose becomes

* The Bavarian maas is equivalent to 1·25 English quart.

apparent by the evolution of bubbles of carbonic acid gas, which forms a wreath of white froth at the edge of the vessel. In another twelve hours larger quantities of a more consistent froth are formed, causing the surface of the liquid to exhibit a very peculiar appearance, which might be compared to that of irregular masses of broken-up rocks; at the same time a more vivid evolution of carbonic acid takes place, and becomes perceptible by the smell. The German term for this phase of the fermentation, *das Bier steht im Kräusen*, can hardly be expressed in English, but the meaning is the fermentation is in full force; these phenomena continue, with a regularly proceeding fermentation, in full activity for from two to four days, and then gradually subside, there remaining on the surface of the liquid a somewhat brown-coloured film of froth, much contracted, and chiefly consisting of the resinous and oily constituents of hops.

The yeast formed is only to a very small extent present on the surface of the liquid, as, in the case of sedimentary fermentation, the carbonic acid evolved cannot carry the isolated yeast-cells to the surface. The temperature of the fermenting liquid increases at the beginning of the fermentation, so that the liquid becomes several degrees warmer than the air of the locality where the fermenting vats are placed. By the fermentation the wort loses the greater portion of its dextrose, about half of which is evolved in the shape of carbonic acid, while the remainder is converted into alcohol; further, a portion of the albuminous substances dissolved in the wort is rendered insoluble, and deposited in the shape of yeast. On being tested with the saccharometer, the liquid—for reasons just explained—exhibits after fermentation a less degree of strength than before. The difference in percentage shown by the saccharometer before and after fermentation is in direct proportion to the quantity of dextrose decomposed, and provides a means of ascertaining the course of the progress of the fermentation. If this difference be made the numerator of a fraction, the denominator of which is the percentage indicated by the saccharometer before fermentation, the value of the fraction will increase proportionately with the completeness or efficacy of the fermentation; if, for instance, a wort before fermentation marks a saccharometrical percentage of 11·5, and afterwards gives 5 per cent., the difference (6·5 divided by 11·5) gives the co-efficient 0·565; that is, of 100 parts of malt extract 56·5 per cent. are decomposed during fermentation.

After-fermentation in the Casks.—After the chief fermentation is completed, which for summer or lager beer requires nine to ten days, and for winter or schenk beer seven to eight days, the young or *green* beer is put into barrels, after having become quite clear by the separation of the yeast. Before the beer is vatted the scum present on its surface is removed. The yeast, settling to the bottom of the vat in which the fermentation took place, consists of three layers, the middle being the best yeast; the lowest, decomposed yeast and foreign matter, is mixed with the yeast of the upper layer, and if not otherwise saleable is sometimes employed in the distilleries of malt spirits. The middle layer serves for further fermenting operations. In breweries where pure water (the reader should bear in mind that Bavaria is alluded to) is not to be had, this yeast is occasionally obtained fresh from other breweries. It is usual to fill casks or vats with winter beer at once quite full; but as regards summer beer several brewings are mixed in smaller vats in order to obtain a uniformly coloured mixture. The barrels are usually coated with pitch on the inside, the aim being to prevent the beer soaking into the wood, and thus giving rise, when the cask is emptied, to the formation of acetic acid. For the after-fermentation, the beer is placed in stone cellars, which should be kept at the lowest temperature practicable, so as to cause the after-fermentation to proceed as slowly as possible, and thus admit of the beer being kept until the brewing season opens.

In all parts of Germany, but mostly so in Bavaria, great attention is paid to the construction of the cellars: these cellars are often excavated in rocks, and sometimes ice-pits are placed in the cellars to keep them very cool. The after-fermentation of the beer sets in when it is vatted, the moment of the beginning of this process partly depending on the condition of the beer when vatted and partly upon the temperature of the cellar. The after-fermentation, which becomes manifest by the appearance of a bright white-coloured foam at the bung-hole, may set in immediately after the vatting of the beer, or may only become perceptible some eight days after. Should the beer happen not to exhibit any sign of incipient after-fermentation, green, young, or new beer is added for the purpose of inducing this process. When the after-fermentation is finished, the bungs of the casks or tuns are not tightly fastened, and the beer is left in this condition (in the cellars, of course) during the summer months. About a fortnight before the beer in the casks is intended to be tapped, the bungs are tightly closed in order to cause as much carbonic acid to accumulate in the fluid as will occasion the beer to foam on being tapped; but if beer happens to be vatted in very green condition, the bung-hole should not remain closed for so long a period, because then so violent a fermentation may set in that, on tapping the cask, its contents become too much agitated, and thereby a very turbid beer (full of yeast) is served to the customers. Sometimes the addition of liqueur (a solution of white sugar) is resorted to for the purpose of setting up a strong fermentation in very old beer. According to J. Gschwändler (1868), beer obtained by the processes alluded to has the following composition:—

Beer.	Decoction.	Bock.	Sedimentary Method.	Infusion.
Alcohol	2·810	3·380	2·940	3·130
Sugar	1·580	2·320	1·460	1·330
Dextrine	4·610	6·910	4·770	4·800
Nitrogenous substances	0·380	0·740		
Other constituents	0·380	0·400	0·890	0·550
Sp. gr. of solution of extract	1·022	1·042	1·028	1·026
Extract (direct estimation)	6·570	9·980	6·230	6·130
„ (according to Balling)	6·950	10·380	7·120	6·680

Surface Fermentation.—Surface fermentation is that induced in the worts intended for the brewing of the bottled beers of North Germany, Bohemia, Alsace, England, and Belgium. Beer obtained by this process of fermentation is not so lasting as that prepared by the sedimentary fermentation process. This difference is due to the fact that the surface fermentation goes on at a higher temperature, proceeds more rapidly, while the elimination of the nitrogenous compounds is also less complete. The reason why this process is preferred to the sedimentary fermentation process is that brewing by the application of the last process is so greatly dependent upon a low temperature that this mode of brewing cannot be continued throughout the whole year, while, as regards the other process, it may be continuously carried on, and the stock of beer kept ready for use can thus be considerably decreased. Surface fermentation, however, is the only plan for preparing briskly foaming and strong beers. Porter, stout, and ale could be brewed as well by the sedimentary method—although in the English climate this process would be more difficult to conduct successfully—but the main reason why the surface fermentation is employed for English malt liquors is that this method, by the great saving of time, is cheaper. The phenomena of the surface fermentation are similar to those of the sedimentary, with the exception that the progress is by far more violent, the froth surging more to the surface of the wort. The yeast is employed in the same manner. An ingenious contrivance is adopted in the London breweries for the purpose of carrying off the yeast from the beer after it has undergone the process of fermentation. The wort is placed in large hogsheads, or *rounds*, the tops of

which are fitted with wooden troughs. Into these troughs the yeast runs as it rises, and is carried away. The beer now becomes clear, and is pumped into the stone vats.

Steam Brewing.—The extensive application of steam to the manufacture of beet-root sugar and alcoholic spirits has given rise to many suggestions for the substitution of heating by steam for direct firing in brewing. The heating is effected by a system of tubes similar to that described in the preparation of beet-root sugar (see p. 705). In brewing, however, though much would be gained by uniformly heating the worts, and by reducing the chances of burning, there would not ensue any great economising of fuel, though much labour might be saved. Steam could not be employed directly without a series of tubes, as the condensation would cause a great dilution of the mash.

Constituents of Beer.—The constituents of a normal beer prepared from malt and hops (not from substitutes) are:—Alcohol, carbonic acid, undecomposed dextrose, dextrine, constituents of the hops (oil and bitter substance, no tannic acid), protein substances, a small quantity of fat, some glycerine, and the inorganic matter of the barley and hops. The acid reaction which a normal beer exhibits after the carbonic acid has been expelled from it by boiling is due to succinic and lactic acids, with traces of acetic acid, and perhaps propionic acid. The sum of all the constituents of a beer after the abstraction of the water is termed the total contents; the sum of the non-volatile constituents, the extractive contents. Beer rich in malt extract is termed rich, fat, or full-bodied beer; and that which is poor in extract, but contains much alcohol, the wort having been rich in sugar which has all been converted, is termed a dry beer.

The proportion of alcohol in beer can be estimated by distillation and the testing of the distillate with an alcoholometer, or by means of an ebullioscope, or with the help of a vaporimeter (see Wine-testing, pp. 724–5–6). The following table shows the average weight per cent. of the alcoholic contents of several beers:—

	Per cent.
Würtzburg lager beer (1870)	4·0–4·3
„ schenk beer	3·3–4·2
Stuttgardt lager beer (1865)	4·1
Culmbach lager beer (1865)	4·5
Coburg lager beer	4·4
Munich lager beer	4·3–5·1
„ schenk beer	3·8–4·0
Bock (Munich, 1870)	4·3–4·8
Porter (Barclay, Perkins & Co., London, 1862)	5·5–7·0
Strasburg beer (1870)	4·21
Vienna beer (1870)	4·1
Rice beer of the "Rhenish Brewery" in Mentz	3·6

The quantity of carbonic acid in beer varies between 0·1 to 0·2 per cent. According to C. Prandtl (1868), dextrose is found in beer in quantities varying from 0·2 to 1·9 per cent. The quantity of dextrine, according to Gschwändler's analyses, varies from 4·6 to 4·8 per cent. The proportion of sugar to dextrine is never constant. The occurrence of protein substances in beer has not been sufficiently investigated to warrant an exact conclusion. It may be said that, on an average, malt extract contains 7 per cent. protein substances, from which Mulder deduces that 1 litre of beer should contain 5·6 per cent. albuminous substances. A. Vogel (1859) found that 1 Bavarian maas (= 1·069 litre) of beer on an average contained 1 to 1·2 gramme nitrogen; and Feichtinger (1864) obtained from 1 Bavarian maas of several Munich beers between 0·467 and 1·248 gramme nitrogen. Succinic acid, acetic acid, and lactic acid occur in Belgian and Saxony beers in large quantities. Tannic acid occurs in Bavarian beers only in small quantity. The inorganic constituents of beer have received great attention.

Martius obtained from 1000 parts of Bavarian lager beer 2·8 to 3·16 parts ash, containing one-third potash, one-third phosphoric acid, and one-third magnesia, lime, and silica. J. Gschwändler and C. Prandtl (1868) found an average extractive contents in 100 parts of—

	Parts.
Schenk beer (Munich)	5·5–6·0
Lager beer (Munich)	6·1
Schenk beer (Würtzburg)	4·6
Lager beer (Würtzburg)	4·4
Bock (Munich)	8·6–9·8
Salvator (Munich)	9·0–9·4
Rhenish rice beer	7·3
Porter (Barclay, Perkins & Co., London)	5·6–6·9
Scotch (Edinburgh)	10·0–11·0
Burton ale	14·0–19·29

100 parts of extractive matter contain, according to A. Vogel (1865), 3·2 to 3·5 parts of ash; 100 parts of ash contain 28 to 30 parts phosphoric acid. 1 litre of beer contains 0·57 to 0·93 gramme of phosphoric acid.

Lermer (1866) subjected several Munich beers to analysis, with the following results:—

	1.*	2.	3.	4.	5.	6.	7.
Specific gravity	1·02467	1·0141	1·01288	1·02	1·02678	1·03327	1·017
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Extractive matter	7·73	4·93	4·37	4·55	8·50	9·63	5·92
Alcohol	5·08	3·88	3·51	4·41	5·23	4·49	3·00
Inorganic constituents	0·28	0·23	0·15	0·18			
Nitrogen—							
In 100 parts extract	11·15	8·71	12·19	8·85	—	6·99	
In 100 parts beer	0·87	0·43	0·53	0·39	—	0·67	

The analysis of the ash of five of these beers gave—

	1.	2.	3.	4.	5.
Potash	29·31	33·25	24·88	34·68	29·32
Soda	1·97	0·45	20·23	4·19	0·11
Sodium chloride	4·61	6·00	6·56	5·06	6·00
Lime	2·34	2·98	2·58	3·14	6·21
Magnesia	11·87	8·43	0·34	7·77	7·75
Iron oxide	1·01	0·11	0·47	0·52	0·84
Phosphoric acid	34·18	32·05	26·57	29·85	29·28
Sulphuric acid	1·29	2·71	6·05	5·16	4·84
Silicic acid	12·43	14·12	7·70	2·86	8·01
Sand	0·83	0·67	2·30	5·20	6·27
Carbon	0·49	0·81	0·40	0·65	0·28
	100·33	101·47	98·03	99·08	98·91

The high importance of beer, both as regards its value as a nutriment and the enormous trade done in this article, has given rise to attempts to find proper and suitable means for testing that liquid in respect of its quality and purity.

Beer-testing.—The experiments proposed for ascertaining the strength as well as freedom from adulteration of beer are termed beer-testing; it is desirable that these operations should be easily executed and yield sufficiently trustworthy results. The strength of the beer is judged according to the quantity of alcohol, extract, and

* 1. Bock beer. 2. Summer beer. 3. White beer. 4. White Bock beer (superficially fermented, obtained by surface fermentation from malted wheat). 5. Another sample of Bock beer. 6. Salvator beer. 7. Winter beer.

carbonic acid it contains; it is evident, however, that the real constituents of the extract—viz., the therein contained quantities of dextrine, hop constituents, the bye-products of alcoholic fermentation, such as, for instance, succinic acid and glycerine, not to mention such substances as glucose and glycerine purposely added to the wort as substitutes for malt—largely influence the quality of any kind of beer, and therefore ought to be determined when any rigorously exact analysis of that liquid is wanted.

Beer-testing is effected partly by ascertaining certain physical qualities of the beer, partly by chemical means. To the former belong its flavour, odour, colour,* consistency, transparency, specific gravity, refractive power to light, &c. By chemical analysis we ascertain and determine the immediate constituents—viz., carbonic acid, alcohol, extractives, and water. The carbonic acid contained in the beer is first eliminated either by repeatedly pouring a quantity of beer from one tumbler or beaker-glass into another, care being taken to let the beer fall from some height, or is removed by shaking the liquid up in a bottle and pouring it out of the same and into it again. The gas having been driven off, the specific gravity of the beer is taken by means of the hydrometer or saccharometer; the beer is next boiled down to half its original bulk; next there is added to it as much water (best distilled) as is required to restore the liquid to its original bulk, and of this liquid the specific gravity is again determined; this will be found greater than that previously obtained. The difference between the two determinations gives the amount of alcohol contained in the beer.

Balling's Saccharometrical Beer-test.—Since, by fermentation, 100 parts of malt extract yield 50 parts alcohol, twice the quantity of alcohol found will indicate the quantity of malt extract necessary for its formation. This quantity of malt extract added to that still existing in the beer indicates the whole of the malt extract existing in the wort before fermentation.

The specific gravity of the beer-wort becomes lower by fermentation, partly because the specifically lighter alcohol is formed, partly by the loss of some of the extractive matter, and partly also by the loss of the substances taken up in the yeast. This decrease of the specific gravity, or *attenuation*, as it is termed, can be estimated either directly by weighing, or by means of the saccharometer. The degree marked by the saccharometer in a beer freed from carbonic acid we will call m; the malt extract of the wort, p. Subtracting m from p, the difference $(p-m)$ gives the *apparent attenuation*, which is the greater the more thorough the fermentation. The quantity of alcohol in a beer varies in direct proportion with the apparent attenuation. The empirical alcohol factor, a, by which the apparent attenuation must be multiplied to obtain the alcoholic contents of the beer = A in weight per cent. $[(p-m)a=\mathrm{A}]$, becomes the greater the higher the original degree of concentration of the wort. For worts between 6 to 30 per cent. of extractive matter, this factor varies from 0·4879 to 0·4588. The alcohol factor can be found by the following equation, when the apparent attenuation $(p-m)$ and the alcoholic contents of the wort (A) are known; then $a=\left(\frac{\mathrm{A}}{p-m}\right)$. With the help of the alcohol factor, a, the alcoholic contents in weight per cent. can be calculated. A quantity of beer being boiled to volatilise the alcohol, and the residue having been diluted with water to the original bulk or weight, if a weighed quantity were operated with, the specific gravity gives the quantity of extractive matter contained in the beer, which Balling terms n. The difference between the extractive matter contained in the wort (p) and that of the beer (n), or

* Very recently, C. Leyser has invented a colorimeter with which, by means of a normal solution of iodine (12·7 grammes iodine to a litre) after having brought the beers to an equal coloration with water, he estimates the relative degree of the original colour. The invention is fully described in the *Jahresberichte der Chem. Technologie* for 1869, p. 467.

$(p-n)$, gives the *actual attenuation*, which, multiplied by the *alcohol factor for the actual attenuation* (b), likewise gives the quantity of alcohol contained in the beer expressed in percentage by weight. The alcohol factor for the actual attenuation is $b=\left(\frac{A}{p-n}\right)$. Subtracting from the apparent attenuation $(p-m)$ the actual $(p-n)$, the difference (d) in the attenuations is obtained—$d=(p-m)-(p-n)$; or $d=m-n$. d is known when the extractive matter contained in the beer (n) and the saccharometrical percentage (m) of the beer free from carbonic acid are known; d is the greater the more alcohol the beer contains. The alcohol factor multiplied by the difference in attenuation gives the percentage (A) of alcohol, from which the *alcohol factor for the difference in attenuation* can be obtained by the following equation:—

$c=\frac{A}{(p-m)}$. It averages 2·24. Finally, with the help of c, the difference in attenuation of the alcoholic contents of a beer can be calculated approximatively, even when the quantity of extractive matter of malt contained in the wort is not known. The apparent divided by the actual attenuation gives a quotient (d), which is the ratio of the attenuations, $d=\frac{p-m}{p-n}$, and can be calculated with the help of the alcohol factor for the apparent attenuation (a) and of the original extractive contents of the wort (p). First—(a) is obtained by the division of the alcohol factor for the actual attenuation by the corresponding attenuation quotient or ratio. Assuming the alcohol factor for the difference in attenuation to be = 2·24, and next doubling the approximative alcoholic contents thus obtained, we arrive at the quantity of the extractive matter of the wort from which the alcohol was formed. Adding to this the extract yet met with in the beer, the sum thus found expresses the approximate percentage of the extractive contents of the wort. When (p) has thus been approximately obtained, Balling's tables give the corresponding attenuation quotient q, reckoning all decimals above 0·5 as units, and neglecting those under 0·5. If only the original concentration of the wort (p) is to be calculated, the percentage of the alcohol of the beer may be obtained from the equation to the actual attenuation $A=(p-n)b$. If the degree after fermentation is 9·75 or $(16·29-6·54)$, the saccharometrical percentage (see pp. 748, 759) $=\frac{9·75}{16·29}=0·542$.

THE MANUFACTURE OF SPIRITS.

The industrial production of alcohol has in most countries a different basis and signification, different raw materials, different purposes, and different fiscal regulations and circumstances, all of which have a great influence on the conditions of manufacture. If an alcoholic fluid is submitted to distillation, alcohol and water pass over, whilst the non-volatile constituents of the liquid remain behind in a more concentrated form.

Properties of Alcohol.—The formula of alcohol (as a chemically pure substance) is C_2H_6O, or $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$. It is a colourless, thin, very mobile fluid of 0·792 sp. gr., boiling at 78·3°, while water boils under the same atmospheric pressure at 100°; thus there is afforded a means of ascertaining, by the boiling-point of an alcoholic fluid, the quantity of alcohol contained. Between 0° and 78·3° (its boiling-point) alcohol expands 0·0936 of its volume, while the co-efficient of expansion of water between the same degrees is 0·0278. The expansion of alcohol is thus $3\frac{1}{3}$ times greater than that of water; and this fact is made available in alcoholimetry. The tension of the vapour of alcohol

at 78·3° is equal to an atmosphere, while water must be raised to a temperature of 100° to obtain the same pressure. Thus, the variation in height of a column of mercury subjected to the pressure of these vapours may be made a measure of the quantity of alcohol contained in a fluid. On this principle the vaporimeter (see p. 724) is constructed. Alcohol is readily inflammable, and burns with a pale blue flame without giving off soot. Its heat of combustion corresponds to 7183 units of heat. It eagerly absorbs water, and upon this property is based its use for the preservation of articles of food, cherries and other fruit, and also anatomical preparations. It mixes with water in all proportions, whereby a decrease of bulk of the mixture and increase of specific gravity is observed—

53·9 volumes of alcohol, with
49·8 „ water, form a mixture, not of

103·7, but of 100 volumes.

Alcohol is a solvent for resins (upon which property is based its application to the manufacture of varnishes, cements, and pharmaceutical preparations), and also a solvent of many essential oils. These solutions are employed either as perfumes, such as eau de Cologne, or as liqueurs, cordials, and aqua vitæ, or as spirits for burning in lamps, as, for instance, the mixture of oil of turpentine and alcohol, so-called fluid gas; alcohol also dissolves carbonic acid gas, a property made available in the making of effervescing wines.

By the influence of certain oxidising agents, alcohol is converted first into aldehyde and next into acetic acid, as illustrated in the so-called quick vinegar making process. Alcohol does not dissolve common salt, and upon this property Fuchs's test is based.

By the action of most of the stronger acids, aided by heat, alcohol is converted into what are termed ethers; as regards the action of sulphuric acid upon alcohol, it depends upon the relative quantities and degree of concentration of these liquids whether sulphovinic acid, ether, or bicarburetted hydrogen gas be formed. Hydrochloric acid forms, with alcohol, ethyl chloride or hydrochloric ether. Butyric and oxalic acids form ethers directly when heated along with alcohol; but most of the other organic acids require the aid of sulphuric or hydrochloric acid for this purpose. Alcohol is the intoxicating principle of all spirituous liquors.

Raw Materials.—Alcohol is always the product of vinous fermentation. The manufacture of spirits therefore includes three principal operations:—

1. The preparation of a saccharine fluid.
2. The fermentation of this fluid.
3. Separation of the alcohol by distillation.

All saccharine fluids, therefore, or those substances which yield alcohol by fermentation, can be employed in the manufacture of spirit; and all materials so employed contain already either completely formed alcohol, or cane sugar and dextrose, or, finally, substances which by the influence of diastase or dilute acids are converted into dextrose. Such substances are starch, inuline, lichenine, pectin compounds, and cellulose. The raw materials of spirit manufacture may be generally classed in the three following groups:—

1st Group.—Fluids in which the alcohol is already present, requiring only distillation to effect its separation. Such fluids are wine, beer, and cider.

2nd Group.—Substances, either solid or liquid, which contain sugar, which may be either cane sugar, or dextrose and levulose, or sugar of milk. In this group are included the sugar-cane, beet-root, carrot, maize stalk, the Chinese sugar-cane (*sorghum*), some kinds of fruit—viz., apples, cherries, figs—some berries (grapes, mountain ash berries, &c.), the melon and gourd, some fruits of the cactus tribe, the molasses of cane

and of beet-root sugar manufacture, the marc of grapes and refuse grain of beer making, honey, and milk.

3rd Group.—All substances which originally contain neither alcohol nor sugar, but the constituents of which may be converted into sugar and dextrose. Such are starch, inuline, lichenine, pectin compounds, and cellulose, chiefly found in—

(*a*) Roots and bulbs: Potatoes, dahlia roots, &c.

(*b*) Cereals: Rye, wheat, barley, oats, maize, and rice.

(*c*) Leguminous and other seeds: Buck-wheat, millet, black or negro millet, peas, lentils, beans, vetch, chestnut, horse-chestnut, oak leaves, &c.

(*d*) Substances containing cellulose: Sawdust, paper, straw, hay, leaves, osiers, moss.

In the future a—

4th Group may be added, which will embrace all substances which probably may enter into the synthetic preparation of alcohol, and thus form what might be called a mineral spirit. Berthelot in 1855 proved that alcohol can be formed from olefiant gas and water ($C_2H_4 + H_2O = C_2H_6O$). Olefiant gas, when agitated for a length of time with concentrated sulphuric acid, gives rise to the formation of sulphovinic acid: and from this liquid, after having been diluted with water, a dilute alcohol can be distilled. This experiment has as yet only a scientific interest; the process has been tried on the large scale in France, but failed to be commercially available.

For the conversion of the starch of potatoes, &c., into maltose, diastase is employed. The production of malt for the distiller differs little from that of a malt for brewing. For the purpose of distilling, it is necessary to produce a malt which is able to split up a maximum of starch into maltose and dextrine. It is, therefore, the object of the distillery maltster to produce a maximum of diastase in the sprouting barley and to bring it into a state of efficacy.

Saccharification.—As has been explained above, when starch is split up by the action of diastase at temperatures below 75°, there are formed diastase and dextrine; this process is saccharification. By the action of dilute sulphuric acid upon starch at higher temperatures there is formed, along with dextrine, chiefly dextrose, and also small quantities of maltose. By the prolonged action of sulphuric acid much—though not all—of the dextrine changes into dextrose. The dextrine which is formed from starch by the action of diastase may be regarded as non-fermentable in the short time allowed for the alcoholic fermentation in distilleries, and yet during the fermentation it is converted into a fermentable sugar—as appears from the experiments of Delbrück and Märcker—by the subsequent action of the residual diastase. When, therefore, the fermentable maltose has been used up by the yeast, the residual diastase converts the dextrine into maltose. For the exhaustion of the fermentable material it is therefore necessary to retain diastase in the mash for alcoholic fermentation. The secondary action of the diastase is disturbed by too high a temperature and by lactic acid in the fermenting mash.

Mashing Process.—The mashing process was formerly carried on in distilleries in the same manner as in breweries. The new methods are based upon the use of steam under pressure, and have been developed in different directions by Hollefreund, Bohm, and Henze.

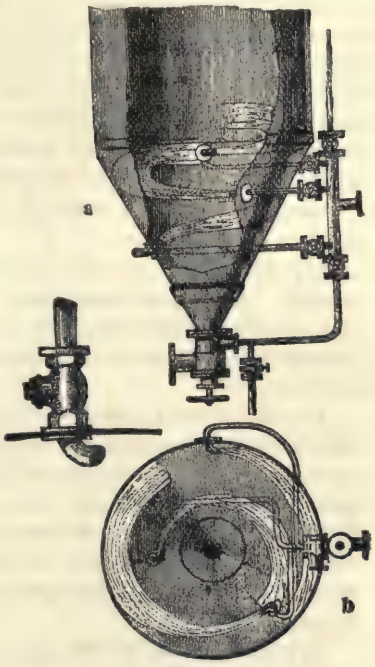
All these new mashing processes aim at a simplification of the operations, a better utilisation of the raw materials, perfection and certainty in execution, or (like the apparatus of Henze) simplification in the saccharification. The apparatus of Hollefreund consists of a horizontal vessel resembling a steam boiler, and for a fermenting space of 4000 litres it must have a capacity of 6000 litres. The potatoes—3000 kilos. for the above capacity—are introduced through a man-hole, and heated by direct steam

after the apparatus has been closed, until the temperature reaches 137° to 143°, which answers to a pressure of 2 to 2½ atmospheres. An agitator, consisting of knives placed spirally around a shaft, is set in action to comminute the potatoes. The steam is then blown off by opening a valve, and the temperature is let sink to about 160°, a degree, however, which would still destroy the diastase in the malt which is now added. An artificial refrigeration is therefore needed. As soon as the pressure in the mashing-pan has fallen to 1 atmosphere the valve is closed, and an air-pump connected with the apparatus is set in action which causes the contents to boil and water to evaporate. By a powerful air-pump it is possible in fifteen minutes to reduce the temperature from 106° to 65°. The rarefaction of the air serves to suck the bruised malt into the apparatus and effect saccharification in a very short time.

Bohm's apparatus consists of a pan in which the potatoes are steamed. The apparatus works without an air-pump, and effects refrigeration by a combined agitating and cooling arrangement. The agitator consists of flat cylindrical vessels of sheet-iron, fitted on their surfaces with knife-like projections, in order to comminute the potatoes. The sheet-iron cylinders are fixed on a hollow axle in such a manner that the cooling water passes through the cylinders and escapes through a double tube in the hollow axle. The apparatus is cooled from without by sprinkling with cold water.

Both apparatus require a great mechanical power, and have been almost completely superseded by that of Henze, a cylinder of strong boiler-plating, provided with a manometer and a safety-valve. It is filled with potatoes through a man-hole in the cover; steam is introduced through pipes, one of which opens underneath the cover, and the others in the lower conical part, until all the air has been expelled through the open safety-valve, which is then closed, and a pressure of 2 to 3 atmos. is given. After the steaming process, the lower valve is opened, so that the potatoes are forced out in a state of fine division. They then arrive in a preliminary mashing-tub, cooled by means of water; they meet here with the needful supply of malt, and are easily liquefied. Greatly to be recommended is the method of admitting steam introduced at Biesdorf, which sets the mass in rotatory movement. In order that the steam may move spirally upwards, the inlet-pipe, *c* (Fig. 522), is turned upwards.

Fig. 522.



According to the experiments of Maercker and Delbrück on the action of the modern steaming apparatus, the starch of the fresh potato floats in a watery liquid, as shown in the section (Fig. 523) of a potato magnified 400 times. The intercellular substance, consisting of matters resembling pectine, which connects the several cells, is insoluble in cold water, but is readily converted into soluble substances in boiling water under pressure. Fig. 524 shows the cells of a potato steamed at 3 atmospheres; the starch granules are completely swelled, and the intercellular matter is perfectly dissolved; the cells still hang together, but they are easily separated if they have not all burst.

The further continuation of this part of the subject would be superfluous where, as

in Britain, the distiller does not operate upon roots, but upon either grain or saccharine matter.

Fig. 523.

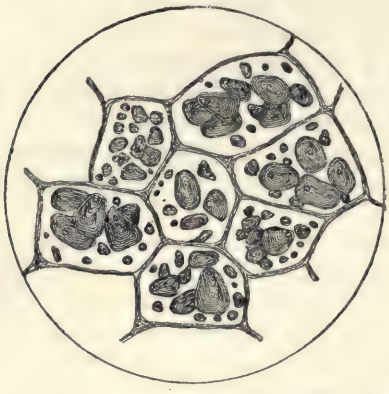


Fig. 524.



Preparation of a Vinous Mash.—Vinous Mash from Cereals.—Grain brandy (corn brandy) may be prepared from either wheat, rye, or barley. Generally more than one kind of grain is used, because experience has proved that a larger quantity of alcohol is obtained when two kinds of grain—for instance, wheat and barley, rye and barley—are mixed. A mixture of rye with wheat or barley malt, or wheat with barley malt, is very generally used, at least abroad. To 1 part of malt from 2 to 3 parts of non-malted grain are usually taken. Either, as is done in England, wort is made, the grain being first malted, next mashed, and the wort drawn off, or the mixture of malt or unmalted grain is allowed to ferment together. The latter method is more usual in Germany, and will be that described here. In Russia and Sweden brandy is prepared without malting; by properly mashing rye-meal a reaction ensues between its constituents, the effect of which is the same as if it had been acted upon by diastase of malt.

The preparation of a mash from grain may be considered as consisting of the following four operations:—

(1) *The Bruising.*—The materials, malted as well as unmalted grain, are first bruised. As it is not essential in the manufacture of spirits that a clear wort should be prepared, the grain may be broken up very small, whereby the formation of sugar is rendered more complete. Green malt is now generally considered preferable by many distillers.

(2) *The Mixing with Water.—Making of Mash.*—This operation is almost identical with that of the mashing of the brewer; the only distinction being that the distiller aims at the entire conversion of the starch into glucose, while the brewer does not require this, as he also wants some dextrine. The complete saccharification, and next the complete conversion of the glucose into alcohol during fermentation, are possible only with a certain degree of dilution of the mash. The quantity of water to be mixed with the grain must not be reduced too much, because that would involve a loss of spirits.

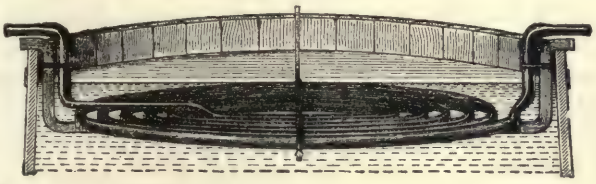
(3) *The Cooling of the Mash.*—When the saccharification is complete, the mash should be rapidly brought to the temperature suitable for fermentation by being placed in cooling vessels, just as is done with the wort in brewing, by being placed in an apparatus termed a refrigerator, or by the application of ice or cold water. The temperature to which the mash has to be cooled varies according to the locality and the duration of the fermentation, but it averages 23° C. When sufficiently cooled the liquid is placed in the fermenting vats.

(4) *The Fermentation of the Mash.*—The fermentation vat is generally made of wood,

though sometimes stone is used. The first possesses the property of retaining the heat for a longer time, and, for the same reason, large vessels are preferred. The capacity seldom exceeds 4000 litres. Either beer yeast in its fluid condition or dry yeast is used to set up fermentation. The latter is mixed with warm water before being added to the contents of the fermentation tanks. Of the fluid beer yeast there are usually taken to 1000 litres of mash 8 to 10 litres; while for 3000 litres of mash 15 to 20 litres of yeast are a sufficient quantity. Of the dry yeast, ½ kilo. is employed to 1000 litres of mash, or 1 kilo. of yeast to 3000 litres of mash. In large distilleries artificial yeast is sometimes employed, as beer yeast of the requisite quality cannot always be procured at a remunerative price. The mode of adding the yeast is the same as that employed in breweries. After standing for from three to five hours the temperature of the mash will have increased to from 30° to 32°. Carbonic acid is then given off, and the heavier substances settle to the bottom of the tank. This continues for about four days, when the clear fluid may be considered ready for further operations.

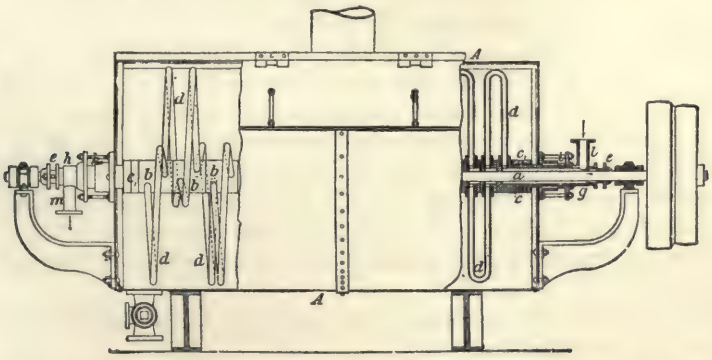
The yield of alcohol is better if the temperature is reduced to 27°–28°. It is therefore prudent to suspend in the cooling-beck a copper refrigerating worm traversed by cold water, as shown in Fig. 525.

Fig. 525.



An apparatus for cooling introduced by Eckert is shown in Fig. 526. The agitators, formed as U-tubes, can be easily taken to pieces. In the front sides of the vat, *A*, is fixed the shaft *a*, upon which are arranged within the vat a number of hollow rings, *b*. At the ends

Fig. 526.



of the shaft *a* there is fixed a rather longer ring, *c*, provided with a screw thread. Upon this thread two female screws, c_1, are cut, so as to hold the rings, *b*, fast together. Each of the rings, *b*, has two radial perforations, in which threads are cut, and in which a number of U-tubes, *d*, are screwed, and connected by concentric rings in such a manner that the ends of each tube, *d*, open into two rings, *b*, lying side by side. Thus all the rings and tubes form with the shaft a system which can be set in motion. This system of pipes effects an energetic mixture of the mass in the vat by means of its curvature. In order to effect an afflux and reflux of the water for cooling, a pipe, *g* or *h*, is pushed upon the shaft *a*, over the rings, *c*. This pipe is closed by the stuffing-boxes, *e*. Both tubes, *g* and *h*, are fitted with short pieces, *l* or *m*, of which the former effects the influx of the cooling water and the latter its outflow.

Spirits from Sugar Waste.—In India the scum from the boiled sugar, the molasses, &c., are brought to fermentation and the fermented fluid distilled. The product is in the English colonies known as *Rum*, in Madagascar and Mauritius as *Guildine*. The peculiar aroma of rum is contained in the portion which first distils over. By the fermentation and distillation of the scum from the boiling of the sugar-cane juice, a coarse, sour, dark brown or black-coloured, acrid-tasting brandy is obtained; it is known as *Negro rum*. In England and Germany rum is frequently made from the diluted molasses of the sugar refineries fermented with yeast, the fermented fluid being distilled after about three or four days' fermentation. The aroma peculiar to rum is obtained by the addition of some pelargonic ether or essence of pine-apple. Beet-root molasses is also largely used for the purpose of obtaining spirits. By itself the beet-root sugar molasses is difficult to ferment, but if the alkalinity of this material is first neutralised by the addition of some sulphuric acid, and the material next boiled with a further addition of acid for the purpose of converting into inverted sugar the cane sugar it yet may happen to contain, the fermentation may be readily set up and regularly proceed. 100 kilos. of molasses yield on an average 40 litres of spirit. The very objectionable odour of this spirit is due to fusel oil, which contains small quantities of propylic, butylic, and amylic alcohol, pelargonic acid, and caprylic acid, while later researches have added to this list œnanthic, caproic, and valerianic acids. The residue left in the retort is used for the preparation of potassa (see page 291). The addition of sulphuric acid has not only the effect of converting the cane sugar into an easily fermentable sugar, but also prevents the setting up of lactic-acid fermentation.

Spirits from Wine and Lees.—The distillation of spirits from wine is chiefly carried on in France, Spain, and Portugal. The yearly production of spirits from wine or French brandy (*alcool de vin*) in France alone amounts to 450,000 hectolitres of 85 per cent. and 400,000 hectolitres of 60 per cent. The quality of the spirit is indirectly affected by the degree of ripeness of the grapes, and directly by the care bestowed upon the fermentation and distillation, by the more or less intimate mixture of the volatile principles of the wine with the alcohol, and by the age of the wine. Old wine yields a spirit of better quality than new wine. The freshly distilled brandy is colourless, and remains so even when bottled; but since the spirit is kept in oaken casks it extracts therefrom some colouring and extractive matter. The best kinds of brandy are distilled in the Département de Charente, and the brand known in commerce as *Cognac* (name of a town) is the most valued. From the marc and wine-lees spirit is also distilled. By the distillation of spirits from wine a residue is left in the retort (the *vinasse*) which contains a large quantity of glycerine, which may thus be obtained as a bye-product.

Since the invasion of the phylloxera the amount of spirit distilled from wine has sunk to about 15,000 hectolitres (1885).

Fermentation.—The addition of yeast to the cooled mash in the fermenting vat takes place in the same manner as with malt. To 100 kilos. of mash are added 1 to 2 litres of beer-yeast, or $\frac{3}{4}$ to 1 kilo. of dry yeast. The potato mash contains, besides the husks of malt and grain, some finely divided cellular tissue; these substances during fermentation are carried to the surface of the mash and form a scum, the appearance and behaviour of which give an opportunity of judging the progress of the fermentation. The fermentation is said to be regular or irregular; the former begins some four to six hours after the yeast has been added, and proceeds in a regular manner, the end depending upon the quantity of yeast added and upon the temperature. The progress is quiet, not violent, the scum which appears on the surface sinking or being drawn to one side of the vat and thrown up at the opposite side, while bubbles of air or gas appear and burst on the surface, much as bakers' dough heaves under the

influence of the ferment. Irregular fermentation is so far opposed to the former that the surface of the mash is only partly covered with froth, which remains in one position, and does not move of itself. The result of such a fermentation is generally defective, the reason being the incomplete saccharification of the mash, the addition of too small a quantity of yeast, or, finally, working at too low a temperature. After about sixty to seventy hours with a regular fermentation, the mash is ready for distillation. Recently, large quantities of spirits have been prepared from maize and also from rice.

Distillation.—The fermented mash (as obtained from potatoes) is a mixture of non-volatile and volatile substances. To the first belongs the fibre, malt husks, inorganic salts, protein substances, undecomposed and decomposed yeast, succinic acid, lactic acid, glycerine, &c.; to the volatile, the alcohol, fusel oil, water, and small quantities of acetic acid. The volatile constituents of the mash, the products of the fermentation, are separated from the non-volatile by distillation, during which the volatile constituents are converted into vapour, afterwards cooled and condensed in another vessel. When a vinous mash is heated to the boiling-point, vapours are generated which consist essentially of alcohol and water; by condensing these vapours there is obtained a mixture of alcohol and water.

Water boils at + 100°, barometer 760 mm.
Alcohol „ „ + 78·3°, „ „

Thus it might be thought that, while the boiling-point of water is 21·7° higher than that of alcohol, it would follow that, when a vinous mash is heated to 80°, only the alcohol would be converted into vapour, the water remaining behind. But this is not the case, for under all circumstances the boiling-point of a mixture of alcohol and water is higher than that of pure alcohol alone, and the vapour formed consists of both alcohol and water. The reason is partly due to the affinity of alcohol for water, partly also to the fact that water evaporates at a lower temperature than its boiling-point; the former (affinity) retains alcohol and prevents its escape at proper boiling-point (78·3°) in the shape of vapour. If the mixture of alcohol and water be heated to its boiling-point (suppose 90°), much more alcohol will be converted into vapour, because its boiling-point is lower, while of water only just so much is evaporated as would be the case were it when pure to be heated to this temperature, while simultaneously a current of air is passed through it, because the vapours of alcohol evolved from the mixture act exactly in the same manner as would a current of air carried through the mixture of alcohol and water, the former substance taking up just as much water as will be volatilised at the boiling-point of the mixed liquids. As the quantity of vapour evolved from a liquid bears a direct relation to the temperature of that liquid, the quantity of aqueous vapours in the mixture of vapours will increase according to the increase of temperature, until at last, as soon as the boiling-point rises to that of water (100°), no more alcohol will be present in the vapours which are given off. At the commencement of the distillation the vapour given off contains much alcohol and very little water; presently more water comes over, and finally only water. It is therefore quite evident that we cannot by distillation separate alcohol at once from the rest of the volatile constituents of a vinous mash liquor. By interrupting the distillation at the proper time, there is obtained in the distillate all the alcohol contained in the mash, along with a certain quantity of water, while the residue of the distillation will not contain any trace even of alcohol. The liquor obtained by the first distillation is generally very weak alcohol, and requires further rectification, as it is termed, to increase the proportion of alcohol. This rectification (another process of distillation) may be continued till the alcohol contains only a small quantity of water, which can only be eliminated by the aid of such substances as have a greater affinity for water than the alcohol, which retains that liquid very tenaciously. Anhydrous, or absolute

alcohol, can only be obtained by treating highly rectified alcohol with some substances which have a great affinity for water, such as caustic lime, fused calcium chloride, &c.; but really absolute alcohol is never used on the large scale in industry. The first portions of liquid obtained by the distillation of vinous mash are rich in alcohol, and are termed fore-run or first-run, while the last portions of the fluid yet containing alcohol are termed after-run. A doubly rectified alcohol contains 50 per cent. pure spirit; but by means of rectification alone a stronger alcohol than of 95 per cent. cannot be obtained. The residue of the distillation is called fluid-wash.

Apparatus for Distillation.—A distilling apparatus as usually employed consists in its simplest form of four parts—namely, the still or retort, the head or cap of the still, the cooling apparatus, and the receiver.

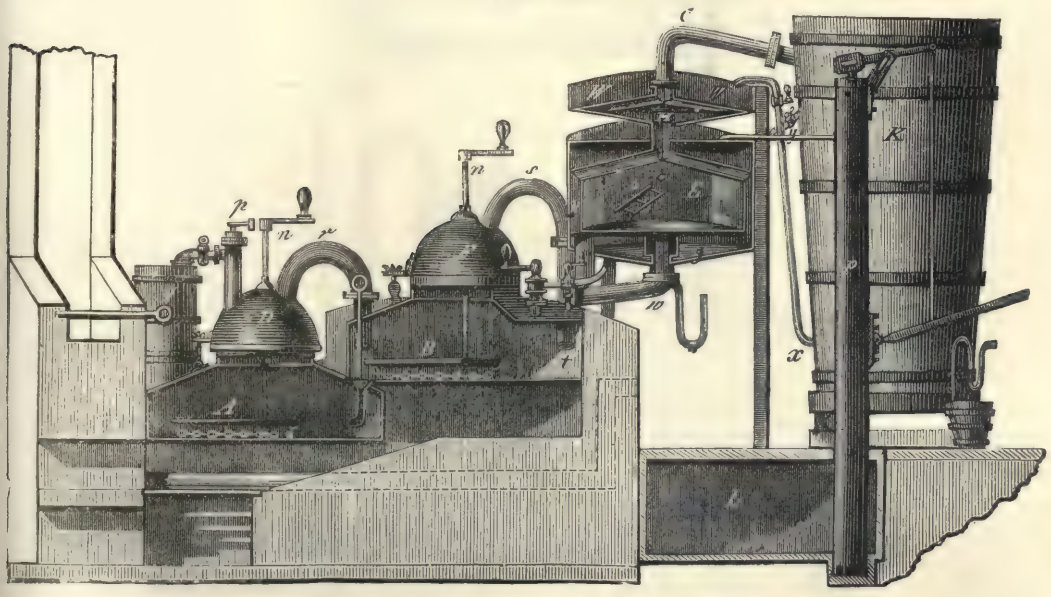
The still or retort is generally constructed of sheet-copper—more rarely, of iron boiler-plates. The shape of the vessel varies, but is generally a somewhat flattened cylinder, provided with a round opening of 12 to 14 inches diameter, fitted with a collar about 1 inch in height forming the neck, on which the cap or head is placed. The bottom of the still is either somewhat bulged inwards at the centre or is quite flat. The residue of the distillation is removed through a waste-pipe fitted with a stop-cock attached to the bottom of the vessel. From the cap or head a pipe conveys the volatilised alcohol to the receiver, while jutting obliquely from the top of the still is a pipe for the introduction of the mash. The head carries the vapours from the still into the cooling or condensing apparatus; although a simple tube might answer this purpose, it is preferred to make the head of the stills large and wide, not only for the purpose of separating any particles of mash which might happen to be carried off with the vapours of the boiling liquid, but also to obtain a distillate richer in alcohol, because an increased surface is favourable to the cooling of the vapours, whereby the aqueous vapour is first condensed; moreover, large heads are advantageous, lest by a rapid evolution of vapours the mash might boil up (priming); roomy space in the head then prevents the liquid passing over into the worm. Since the volume of the vapours decreases during the condensation, a somewhat conically shaped head would be the best form for this portion of the apparatus. The cooling apparatus is not simply destined to convert the vapours carried into it from the head into liquid, but it is also required that this liquid be so far cooled down as to prevent—at least as much as possible—the evaporation of the distillate; the condensing apparatus should not be too roomy; that is to say, there should not be too much space for the vapours, because this would cause air to enter the cooling apparatus, and this air, while mixing with the vapours of alcohol, carries off along with it some of this fluid, thereby causing a loss of the fluid. It is also requisite that the cooling apparatus be strongly made, yet at the same time so constructed as to admit of being readily taken down for cleansing purposes and easily fitted up again; usually the cooling apparatus—technically termed worm—consists of a series of spirally bent tubes made either of block tin or copper, seldom of lead; this apparatus is placed in a large wooden or metal vat containing cold water, or as in the more recently constructed distilling apparatus, cold vinous mash, which is thus made warm previous to being transferred into the still, whereby, of course, a saving of fuel is effected.

The principal improved apparatus which we shall describe are those of Pistorius, Gall, Schwarz, Siemens, and Cellier-Blumenthal.

Pistorius's Apparatus.—Pistorius first introduced in Germany a distilling apparatus fitted with two stills ingeniously connected with rectificators and dephlegmators. When a distilling apparatus is required which not only extracts all the alcohol from the mash, but also produces the alcohol in a very pure and concentrated state, performing this work with the least possible expenditure of fuel and labour, Pistorius's apparatus answers the purpose admirably. *A* and *B*, Fig. 527, represent the two stills.

A is the main still, which is either placed on a furnace and heated directly by fire or by means of steam. Heating by steam-pipes instead of direct firing possesses many advantages. The second still, *B*, is placed at a somewhat higher level than the first, and when not heated by steam-pipes is situated on the flue of the furnace fire of the first still. The main still, *A*, is fitted with a large helm, *D*, fastened on the still with bolts and nuts. *p* is a tube projecting from the helm and provided with a safety-valve which opens inwards, in order to give access to air as soon as a vacuum ensues in the interior of the apparatus towards the end of the distillation in consequence of the condensation of the vapours. There is also connected with this tube, *p*, a small condenser, *q*, as in Dorn's apparatus, from which samples showing the progress of the distillation may be taken. In both stills stirring apparatus, *m* and *n*, are fitted to prevent the mash from burning. By the tube *x* the vapour of the "low wine" is admitted to the second still, the mash-still. From the helm, *F*, of the mash-still a curved pipe, *s*, conveys the vapour to the mash fore-warmer, which, as in Dorn's apparatus, is

Fig. 527.

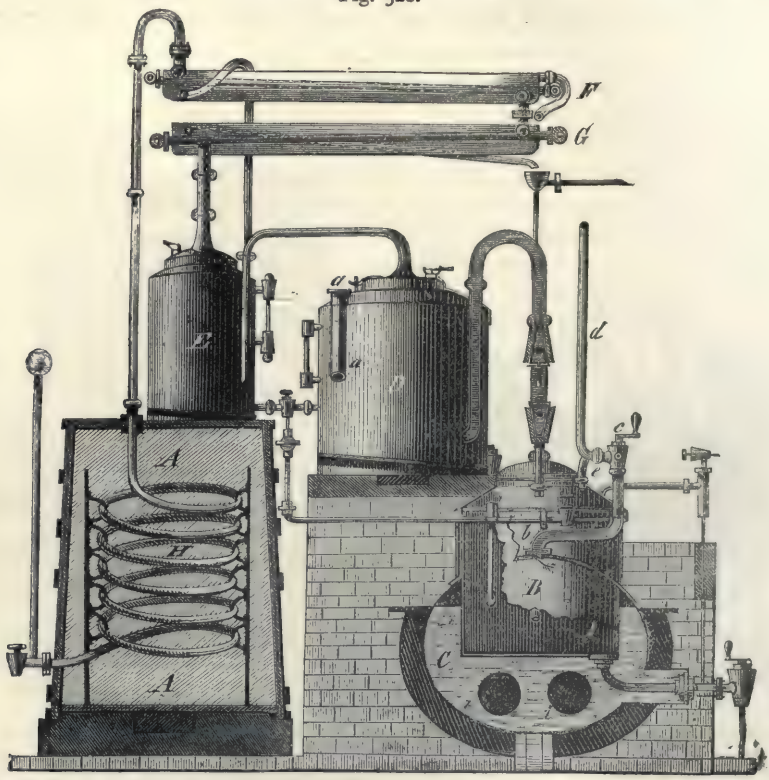


divided into two parts, the upper, *E*, containing the mash, the lower, *g* (the "low wine" cistern), the vapour ascending along the narrow passage, *V*, to the rectification apparatus, *H*. Frequently the vapour is conveyed to a third still before entering *g*; this still is not shown in the drawing. The rectification apparatus, *H*, consists of two or three conically shaped vessels, made of sheet-copper and connected together, and is provided with a cistern filled with water, *W*; it is connected with the condenser, *R*, by the tube *C*. The tube *x* conveys cold water to the rectification apparatus, and the short tube, *y*, does so to the fore-warmer. The pump, *P*, is employed to pump the mash from the cistern, *L*, to the fore-warmer; thence it is carried to the second still, and thence again to the first still. When both stills and the fore-warmer are filled with mash, the fire is lighted under the first still. The steam or vapour from the mash in *A* passes to the mash in *B*, which is thereby heated to the boiling-point. The still *B* serves, therefore, the purpose of a rectificator. When the distillation has begun, the vessel, *W*, on the rectificator is filled with cold water, which is re-supplied when it has become warmed by the passing vapours. As soon as the steam reaches the upper

rectificator, the real distillation commences. The condensed fluid drops into a cistern in which a hydrometer is placed.

Gall's Apparatus.—In most apparatus for distilling from a vinous mash the distillate becomes gradually weaker and is not throughout of the same strength. Gall and Marienbad have endeavoured to avoid this defect in their apparatus, Fig. 528, so as to obtain a more uniform product during each distillation. Two stills are placed in a suitable manner in a steam-boiler and the stills are connected with the separator (low wine cistern). *B B* are the stills; *C* is a boiler with flues, *i i*. The stills, in order to prevent them cooling, are fixed into the boiler. *D* is a third still placed on, not in, the boiler; *E* is the low wine cistern; *F* and *G* two dephlegmators or separators; *A* is a condenser with a worm, *H*. The mash is put first into the still *D* by means of the tube *a a*, this still serving as a fore-warmer and rectificator. From this still both the

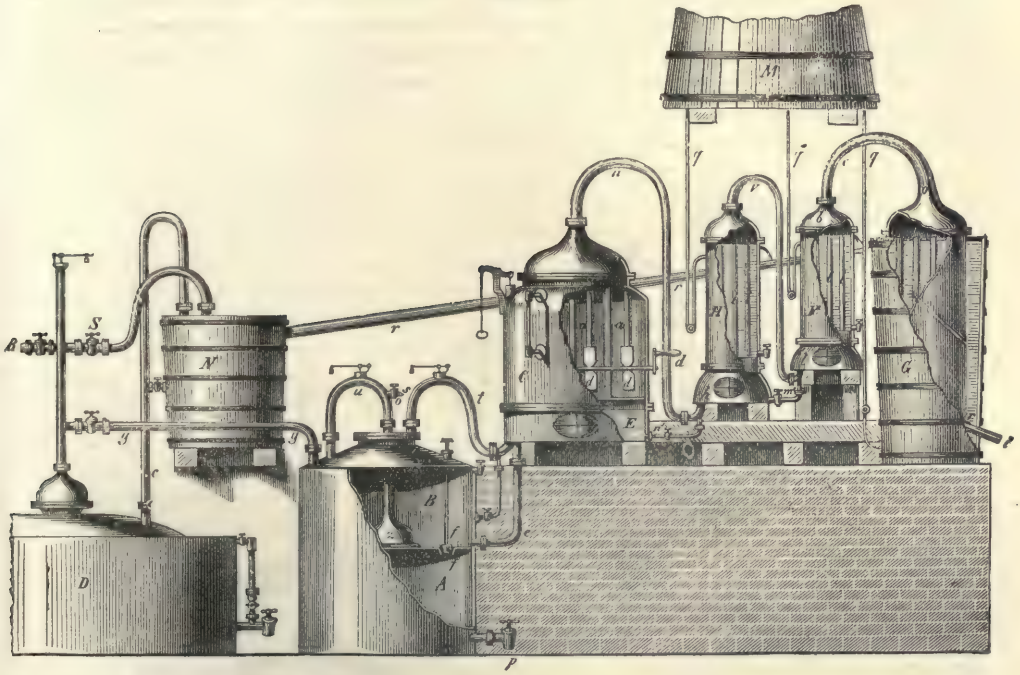
Fig. 528.



stills *B B* are filled. From the boiler a current of steam is conveyed through the bent tube, *b*, into the three-way cock, *c*, whence the steam is either passed into one or both the stills *B B*, or is conveyed upwards by the tube *b* to the vessel destined to steam the potatoes. The vapour from one or both of the stills *B B* proceeds to the still *D*, and thence into the low wine cistern, *E*, and passing through the dephlegmators, *F* and *G*, finally enters into the condenser. The peculiarity of Gall's apparatus consists in that by the peculiar arrangement of tubes and stop-cocks, each of the two stills may at will be brought into action, it being possible to turn the steam at pleasure into the right-hand still, and next into the left-hand still, or *vice versâ*. Each still may be also disconnected, the wash therefrom discharged, and the still re-filled without in the least interrupting the working of the other apparatus of the portions; the distillation can therefore proceed uninterruptedly, one part of the apparatus being filled while the other is at work.

Schwarz's Apparatus.—Schwarz's apparatus is in very general use in the south-west of Germany. It consists, Fig. 529, of the steam boiler, *D*; two mash-stills, *A* and *B*; the fore-warmer, *C*; the "low wine" cistern, or receiver, *E*; the rectificators, *H* and *F*; and the condenser, *G*. *M* is a reservoir for cold, *N* one for hot water. The steam generated in the boiler, *D*, passes through the pipe, *g*, into the under compartment, *A*, of the double still, and through the mash contained there; becoming mixed with vapours of alcohol, it arrives in the helm *z*, and further makes its way by means of the tube *u* into the upper part of the double still; thence, after a double rectification, it is conveyed by means of the tube *t* to the fore-warmer, *C*; the upper part of this vessel, provided with the tubes *a a a*, acts as a dephlegmator or separator, the condensed fluid flowing into *E*. The steam which arrives from the upper part of the still passes through *E*, and thence, by way of the tubes *a a*, into the helm and the tube *n*, which latter is surrounded with the vessel *H*, kept cold by means of cold water; the dephlegmation continues here. From *H* the steam passes through *V* to *F*, an apparatus cor-

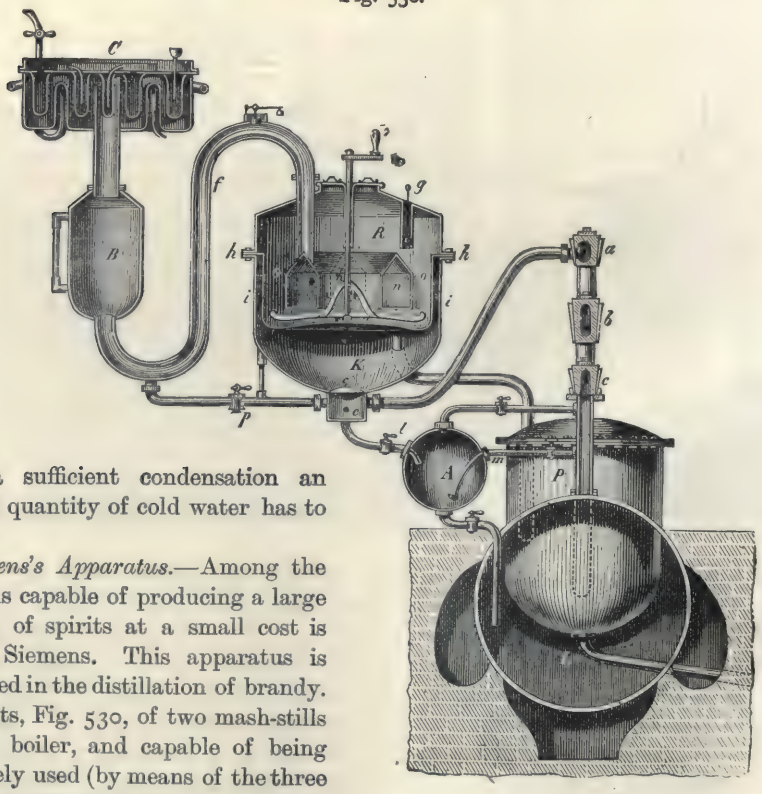
Fig. 529.



responding to the fore-warmer, *C*, but of smaller dimensions, because here the quantity of vapour has become greatly reduced while it has become richer in alcohol. The dephlegmator tubes are here surrounded by cold water, not by cold mash, the former liquid being constantly renewed so as to keep cold. The steam or vapour collected in the helm *b* is sufficiently laden with alcohol to admit of being at once conveyed to the condenser, *G*, the condensed distillate flowing out at *i*. The vinous mash is first poured into the fore-warmer, *C*, wherein it is occasionally stirred by the arms, *d d*, and crank, *d*, so as to keep it uniformly mixed and heated. When the mash has become warm it is conveyed into the upper compartment of the double still by the pipe *e*, and into the lower compartment through the open valve; this compartment also serves as cistern for the phlegma from all other parts of the apparatus; the fluid flows backwards from the compartments *h* and *l* of the rectificators, *H* and *F*, by way of the tubes *m'* and *n*, into the low wine cistern, *E*, thence into the upper compart-

ment of the double still, where it mixes with the mash. As soon as the mash has given up all its alcohol, which can be ascertained by testing the inflammability of the vapour issuing from the test stop-cock, *o*, the residue is removed by opening the tap, *p*. By means of the tubes *q q q*, the rectificators and condensing apparatus are supplied with cold water. The warm water from the condenser is conveyed by the tube *r* into the boiler. By means of *R*, the steam can be admitted to the potato vessel, and by *S* into the reservoir, *N*, when it is desired to heat the water it contains to the boiling-point. Schwarz's apparatus possesses the advantage of being easily taken to pieces and cleansed. But, on the contrary, among its disadvantages are the following :—The construction of the mash-warmers is not quite suited for the purpose, while also the condensed liquid in *E* is not brought sufficiently into contact with the hot steam to effect a thorough distillation or rectification. The steam passes so quickly through the liquid that it is only very imperfectly deprived of its water (dephlegmated) when it reaches the dephlegmation apparatus, where it will consequently be but imperfectly rectified, while the vertical steam-pipes offer too few points of contact, and allow much steam to pass off without being fully condensed; while even the partly condensed vesicular steam is carried off along with the steam escaping condensation. The condenser itself is imperfect, being constructed of a number of vertical pipes, through which the condensed liquid rapidly falls without becoming quite cold, and in order to obtain a sufficient condensation an immense quantity of cold water has to be used.

Fig. 530.



Siemens's Apparatus.—Among the apparatus capable of producing a large quantity of spirits at a small cost is that of Siemens. This apparatus is much used in the distillation of brandy. It consists, Fig. 530, of two mash-stills set in a boiler, and capable of being alternately used (by means of the three cocks, *a*, *b*, and *c*), in the same manner as in Gall's apparatus, while the fore-warmer and dephlegmator is constructed according to Siemens's plan *L* is the boiler; *P* one of the mash-retorts; *K* is the low wine receiver; *R* the fore-warmer; *A*, a reservoir in which the condensed water intended as feed water of the boiler is collected; *C* is the dephlegmator; *B* a reservoir for the

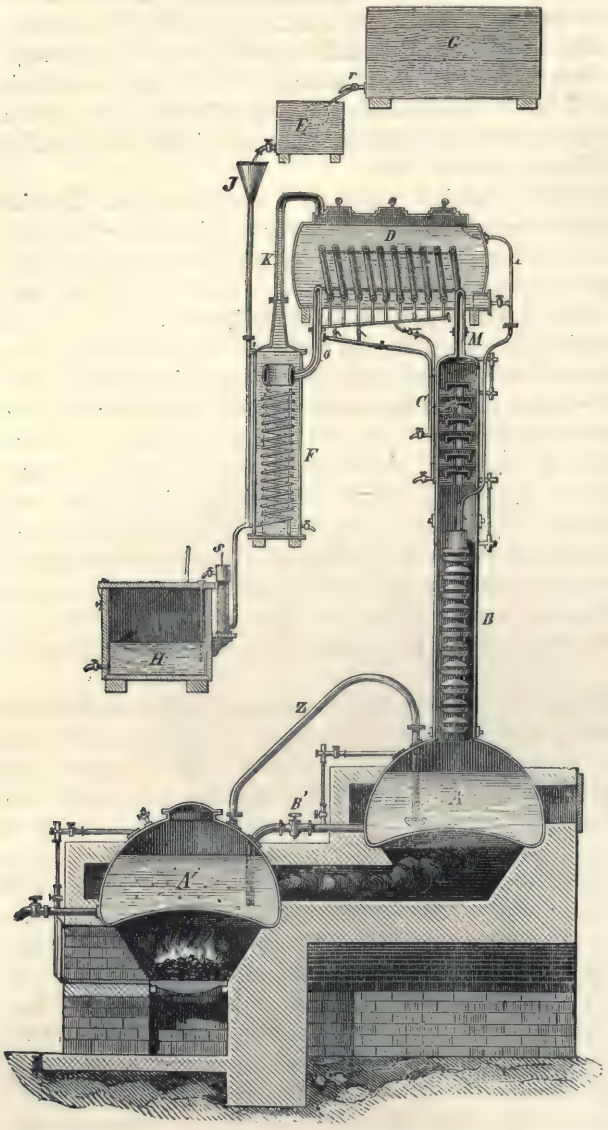
vapours condensed in *C*. From the dephlegmator the vapour passes to a condenser not shown in the engraving. This apparatus is constructed of such dimensions that it can perform the work about to be mentioned. The boiler has to steam about 5000 kilos. of potatoes in four lots, during from forty to forty-five minutes each, and should thus be capable of yielding in three hours the fifth part of the weight of the potatoes, = 1000 kilos., or in one hour 333 kilos. of steam, which renders necessary a steam-generating surface of about 11 square metres. But since the distillation requires steam also, this generating surface has to be increased by about 20 per cent., and should consequently be 13·5 to 14 square metres. The size of the mash-stills should be sufficiently large to contain with ease 500 litres when properly filled; because, as already stated, the fluid from *A* is not returned to the still, but to the steam-boiler, the stills being set into the last-named vessel not becoming externally cooled, whereby the quantity of water carried along with the vapours of spirit is compensated for.

The mash-warmer consists of a cylindrical portion, *i i*, the lower part of which has an indentation, *c*. In the cylinder is placed a narrower portion, *o o*, of the real mash-containing vessel fitted with the heating tube, *f n*. The upper part of the fore-warmer is fitted to the lower part by means of the flange, *h h*. *r* is a stirring apparatus, which is frequently set in operation during the process of distillation. The vapours from the second still are carried into the depression, *c*, under the fore-warmer, which, in order that the vapours may come into contact with the phlegma, is covered with a sieve. The vapours surround the under part of the mash reservoir and enter into the tube *f*, through which they pass to the lower cylinder of the dephlegmator. The condensed water of the dephlegmator is conducted into the reservoir, *A*. The upper and under part of the fore-warmer are made of cast-iron, but the interior bottom and heating surfaces are made of copper. This kind of fore-warmer has the advantage of uniformly distributing the heat, while it can be easily cleansed. The dephlegmator, *C*, is so contrived that the rectified vapour can be conveyed to the condenser by two separate pipes placed in an opposite direction to each other, and are joined again in close proximity to the condenser. The remainder of the details will be seen on studying the drawing.

Continuous Distilling Apparatus.—Among the distilling apparatus intended for the distillation of wine (not of mash), and so constructed as to be fit for continuous working, we must not neglect to mention the apparatus of Cellier-Blumenthal, as improved by Derosne, and represented in Fig. 531. This apparatus consists of two stills, *A* and *A'*; the first rectificator, *B*; the second rectificator, *C*; the wine warmer and dephlegmator, *D*; the condenser, *F*; the regulator, *E*; a contrivance for regulating the flow of the fluid wine from the cistern, *G*. The still *A*, which, as well as the still *A'*, is filled with wine, acts as a steam boiler. The low wine vapours evolved come, when they have arrived in the rectificators, in contact with an uninterrupted stream of wine, whereby dephlegmation is effected; the vapour thus enriched in alcohol becomes still stronger in the vessel *D*, and thence arrives at the cooling apparatus, *F*. In order that a real rectification should take place in the rectificators, the stream of wine should be heated to a certain temperature, which is imparted to it by the heating of the condenser water. The steam from the still *A'* is carried by means of the pipe *Z* to the bottom of the still *A*. Both stills are heated by the fire of the same furnace. By means of the tube *B'* the liquid contained in the still *A* can be run into the still *A'*. The first rectificator, *B*, contains a number of semicircular discs of unequal size, placed one above the other, and which are so fastened to a vertical centre rod that they can be easily removed and cleansed. The larger discs, perforated in the manner of sieves, are placed with their concave surfaces upwards. In consequence of this arrangement the vapours ascending from the stills meet with large surfaces moistened with wine, which, moreover, trickles downwards in the manner of a cascade from the discs, and comes,

therefore, into very intimate contact with the vapours. The second rectificator, *C*, is fitted with six compartments; in the centre of each of the partition walls (iron or copper plates) a hole is cut, and over this hole, by means of a vertical bar, is fastened an inverted cup, which nearly reaches to the bottom of the compartment wherein it is placed. As a portion of the vapours are condensed in these compartments the vapours are necessarily forced through a layer of low wine, and have to overcome a pressure of a column of liquid 2 centimetres high. The fore-warmer and dephlegmator, *D*, is a horizontal cylinder made of copper fitted with a worm, the convolutions of which are placed vertically. The tube *M* communicates with this worm, the other end of which passes to *O*. A phlegma collects in the convolutions of this tube, which is richer in alcohol in the foremost windings and weaker in those more remote: this fluid, collecting in the lower part of the spirals, may be drawn off by means of small tubes, thence to be transferred, at the operator's pleasure, either all or in part, by the aid of another tube and stop-cocks, to the tube *O*, or into the rectificator. By means of the tube *L* the previously warmed wine of the dephlegmator can be run into the rectificator. The condenser, *F*, is a cylindrical vessel closed on all sides, and containing a worm communicating with the tube *O*. The other end of the condensing tube carries the distillate away.

Fig. 531.



On the top of this portion of the apparatus the tube *K* is placed, by means of which wine is run into the dephlegmator. The cold wine flows into the cooling vessel by the tube *I*. When it is desired to work with this apparatus, the first thing to be done is the filling of the vessels *A* and *A'* with wine. The stop-cock, *E*, is then opened, whereby the tube *J*, the condenser, *F*, and the dephlegmator are filled with wine. The wine in the still *A'* is next heated to the boiling-point; the steam enters the tube *Z* and is condensed in *A* until the wine here is heated to the boiling-point by the combined

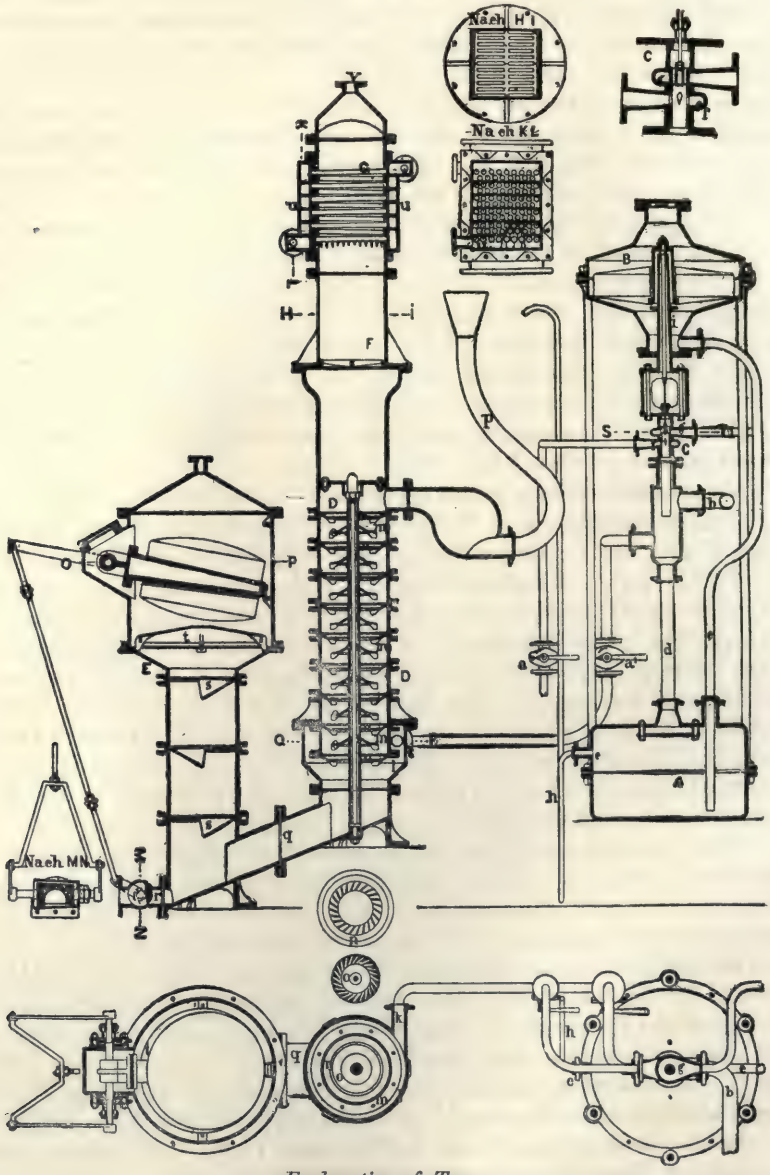
effect of the steam and the hot gases circulating in the flue. The low wine vapour then passes to the rectificator, *B*, and thence into the worm of the dephlegmator, *D*, where the greater portion of it is condensed, the phlegma flowing backwards into the rectificator. As soon as the fore-warmer is so far heated that the hand cannot be kept in the hot wine, the stop-cock of the vessel *E* is opened, and the distillation commences. The wine which is conveyed by the tube *J* into the cooling vessel, *F*, soon begins to become hot, and is then conveyed to the fore-warmer, where its temperature becomes nearly as high as the boiling-point; by means of the tube *L* this fluid is conveyed into the rectificator, *B*, and thence into the still *A*.

As soon as the wine in the still *A'* contains no more alcohol, the stop-cock fitted to the lower part of the vessel is opened, and the vinasse run off at *R*, the still being resupplied by opening the stop-cock *B'*. The vapour proceeds in the same way, but in a reversed direction; when the vapour has been condensed in *F* it is first collected, as alcohol, in the small vessel, *N*, provided with an areometer, and thence conveyed to the cistern, *H*. The strength of the alcohol obtained by means of this apparatus increases with an increase of the number of coils of the condenser placed in the dephlegmator and connected with the rectificator. Practical experience decides, according to the alcoholic strength of the wines to be distilled, and the quantity of pure alcohol desired in the distillate, the opening or shutting of the various stop-cocks of this apparatus. Derosne's apparatus may be readily made continuous; for this purpose it is only necessary to fill the reservoir, condensing apparatus, and rectificator with cold water, while the lower portion of the tube *L* is closed.

Among the recent continuous action apparatus is that of R. Ilge. It consists (Fig. 532) of the steam regulator, A B C, the mash-column, D, the vinasse regulator, E, the rectifier, F, and the dephlegmator, G. The apparatus is chiefly constructed of cast-iron—only the cocks, the steam damper, C, and the support of the float in the vinasse regulator are of brass, the float and the tubes are of copper, and certain rods are of wrought iron. The function of the steam regulator is to reduce to a normal pressure the boiler-steam, which enters through the cock, d, and the engine-steam, introduced through the pipe, b. The body of the still, A, is filled with water up to the short tube, c, which is pressed up by the steam entering by d through the tube e to the float, B. The float, by means of its guide-rod, communicates its movement downwards to the plunger of C. The case of C contains, as shown in the drawing, two mutually superimposed expansions, f and g, each with a short pipe. Four slits in the hollow piston connect, according to the movement of the float, the interior of the piston either with the expansion f or with g, or with neither of the two. As long as the float does not rise, the slits convey the entire steam of the boiler from f. The rise of the float cuts off the steam more and more, and as, at the same time, the escaping steam from the engine streams in through b, the case may occur that the slits are exactly covered by the intervals between the two expansions, or extend beyond the expansion g, and let the superfluous steam escape into the open air. In any case the piston will place itself so that the pressure of the steam is equal to the column of water raised. In order that the steam boiler is not filled with water above L, a tube, h, is inserted through which the steam presses the water up and down without itself escaping. In the mash-column, D, the boiling mash forms a continuous, unbroken column of liquid. From the cock a' the regulated steam enters through the short piece, k, into the space between the vessel l, and the lowest cylinder, m, passes through the vinasse downwards, and streams, equally distributed, in an upper direction into the mash. Ribs are cast on the lower surface of the bottom m, and through their intervals the steam enters the mash in the same direction as the mash. Hereby the liquid is kept in a rotatory movement, and as it arrives at the bottom n with a movement in the opposite direction, a thorough interpenetration of steam and mash is effected. The

ascending vapours collect on the superjacent floor, o, and are led back into the mash by the ribs, but with a rotation to the left, while a rotation to the right was produced by the floor n. The upward passage of the vapours takes the same form; at the floor in the mash is turned to the right, and every floor o to the left. A plentiful distilla-

Fig. 532.



Explanation of Terms.

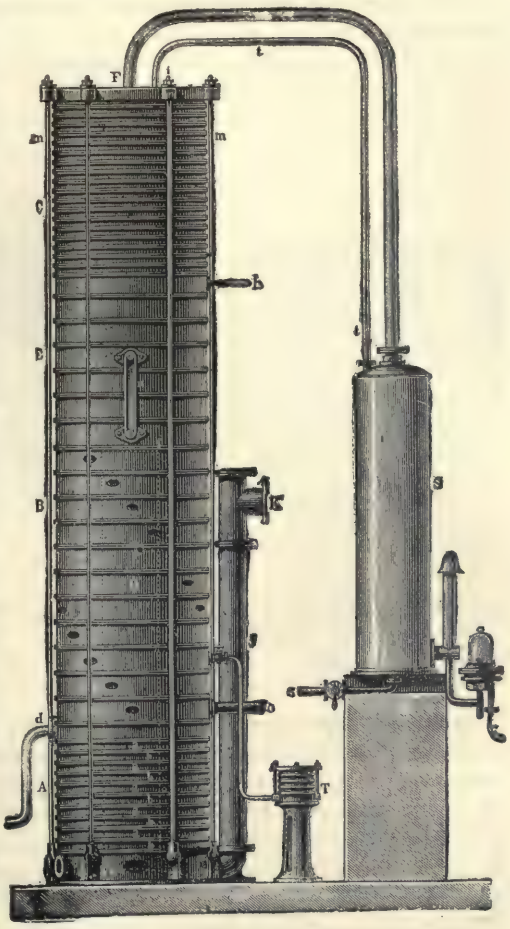
Nach H I	Across Section H I.
Nach K L	Across Section K L.
Nach M N	Across Section M N.

tion takes place by both currents, and also a dephlegmation on the upper floors, where the vapours meet with the cold mash flowing in by the tube p. In the elevation only two ribs are shown, but on the ground floor we see the whole arrangement of the ribs,

seen from below. It appears from the drawing how the floors n are mounted on a wrought-iron rod by means of sheaths, and how the floors n are arranged between two cylinders, m. As the mash-column, D, during working, is filled with mash above its highest floor, o, the vinasse, which had entered into the vinasse regulator, E, through the square channel, q, has risen to the same height in the latter, though less high than in D, as here the mash is specifically lighter than the vinasse. The float in E communicates its upward movement by means of a rod to the vinasse cock, r, and emits through the latter as much vinasse as mash enters through the pipe p. The development of steam from the overheated vinasse (which is perceptible in large works) is rendered innocuous by the floors s, which expedite the vapours upwards, and at the same time present by their conical sections sufficient room for the ascending and descending vinasse. The floor t, resting on four feet, keeps off the vapours from the float.

The ascending vapours come in intimate contact with the liquid dripping down from the dephlegmator, G. The rectifier, F, and the dephlegmator, G, have four-sided sections. F is filled with porcelain balls from the grate up to its upper edge. G contains a number of copper tubes laid almost horizontally in rows, among which the cooling water flows upwards from row to row by means of the two water-covers, u. To each copper tube there are soldered slips of sheet-copper, 30 millimetres in length, 6 millimetres in breadth, and painted below, at intervals of 25 millimetres from each other, as shown in the lowest tube in the figure. The alcoholic vapours rising out of the mash pass through the grate, through the intervals of the porcelain balls, through the intervals of the cooling-tubes, and ultimately through the short tube, v, to the spirit-cooler. Each drop which is formed on the cooling-tubes runs to the next copper slip, falls off from its point to the next tube below, and arrives ultimately at the upper layer of balls, which are uniformly wetted by all the descending drops as they trickle downwards from ball to ball. Rectification takes place on the balls and on the moistened surfaces of the pipes and the slips.

Fig. 533.



In the distilling and rectifying apparatus of Siemens Brothers & Co. the principal parts are:—The preiminary heater, A, the mash-column, B, and the rectifier, C (Figs. 533 to 536), formed of cast-iron pieces, held together by the long bolts, m, and with joints rendered air-tight by means of varnished pasteboard. In working, the chambers b of the preliminary-heater, A, and a part of the support, c, are full of hot vinasse; the chambers a and the remaining part of c are full of cold mash, which

is to be deprived of its spirit, which obtains a preliminary heating by withdrawing a large share of heat from the adjacent boiling vinasse before passing into the de-alcoholising column, B. Accordingly, the mash, which is pumped up at d into the preliminary heater, traverses in succession the compartments, a, of the band, D (Fig. 534), falls down into the piece, c, underneath, and passes through a wide opening into the central tube, D, in which it rises upwards and pours at f into the mash-column, B.

This column, B, consists of a number of pieces, with central tube open at both ends and ring-shaped perforated bottoms (Fig. 535). The space beneath this bottom serves for collecting and receiving the vapours rising from the liquid below, whilst the space above the bottom serves to receive the liquid which has to give up its alcohol. In every one of these nested pieces the liquid to be deprived of its alcohol, in passing through the apparatus, can only flow round in one direction, and not quite round, because a perpendicular rib hinders the annular connection of the liquid, whilst a lower opening makes a connection with the liquid in the next lower compartment. In consequence of this arrangement of the column, the mass is so thoroughly de-alcoholised that the heat can be used over again, and the removal of the alcohol effected at the cost of relatively very little heat.

Fig. 534.



Fig. 535.

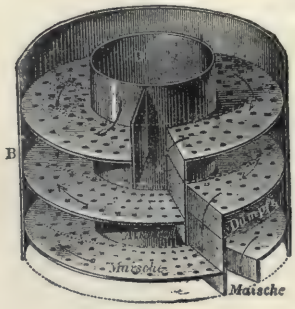
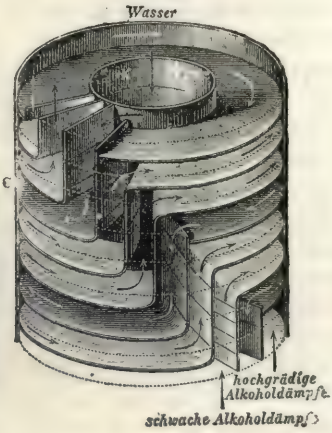


Fig. 536.



Explanation of Terms.

frische Maische	Fresh mash.	*Dämpfe*	Vapours.	*Wasser*	Water.
heisse Schlempe	Hot vinasse.	*Maische*	Mash.	*hochgrädige Alkoholdämpfe:*	Strong alcoholic vapours.
				schwache Alkoholdämpfe:	Weak alcoholic vapours.

From the lowest part of the column, B, the mash, perfectly freed from spirit, passes as vinasse into the preliminary heater, traverses the chambers b, giving off a considerable quantity of heat to the cold mash in the interposed mash-chambers, a, and flows off continuously at K from the vinasse outflow pipe, I. The chambers, a and b, of the preliminary heater having sloping bottoms, both mash and vinasse flow downwards; hence no deposits can be formed in the chambers. Grains, &c., pass into the piece, c, which keeps them back, and is removed every two or three months. The apparatus, when working, is full of mash up to the gauge-glass, n.

The alcoholic vapours liberated from the mash ascend into the rectifier, c. It consists of a number of cast-iron pieces, put together so as to form a way for the vapours rising from the mash-column, B, and partly serve to receive the cooling-water, which deprives the vapours of their excess of heat and facilitates the process of rectification.

The vapours pass at F into the spirit-cooler for condensation, whilst the phlegm formed in the rectifier collects on the floors of the chambers, and, if it is not re-evaporated by the process of rectification, flows back into the mash-column by an internal tube.

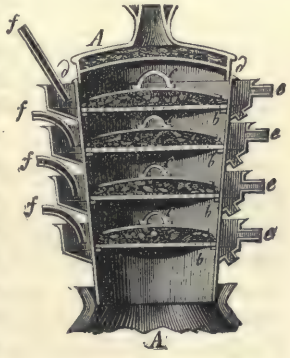
The cooling-water takes its way into the rectifier at i, and flows off at h. It is convenient to let this cooling-water first act on the spirit-cooler, so that it enters the cooler, S, at s, and then flows through the tube t into the rectifier at i.

The sensitive indicator, T, gives an easy and certain indication whether the mash is perfectly de-alcoholised or not. It must be considered that spirit, distilled in cast-iron apparatus, often gets a bad smell and taste, by taking up hydrocarbons and sulphuretted hydrogen.

Purification of the Crude Spirit (*De-fuseling*).—In working up crude spirits there are obtained two products, which contain the impurities. Some of the ethers thus formed exhibit a highly agreeable odour, and are therefore used in perfumery, and for the flavouring of sweetmeats, bon-bons, &c.

As for many of the applications of potato-spirit the fusel oil is a disadvantage, the spirit has to be submitted to an operation of rectification, whereby the fusel oil is got rid of. The suggestions which have been made for this purpose refer either to the destruction of the fusel oil by oxidation or the action of chlorine, or of the masking of the oil and its conversion into less disagreeable compounds; partly also to a real removal of the fusel oil from the spirit. When the fusel oil containing spirit is rectified over chloride of lime (bleaching-powder), potassium permanganate, &c., valerianate of fusel ether is formed. But since the action of these reagents is not limited to the amylic alcohol, but extends to the ethylic, it is very difficult to adjust the quantity of these reagents so that only the amylic alcohol be acted upon. If the spirits from which the fusel oil is to be removed are treated with a mixture of sulphuric acid and vinegar, there is formed, besides some acetic ether, amyl acetate, of a pleasant fruity flavour. Hydrochloric and nitric acids, also used to remove fusel oil, act in a somewhat similar manner. The most approved method of removing the fusel oil is by means of well-burnt charcoal (vegetable charcoal, or bone-black), which, when brought into contact with the crude spirit, absorbs the fusel oil mechanically. By the aid of charcoal, spirits and brandy (when not obtained from wine) are purified either in the state of vapour, or by digestion with the charcoal, and filtration at the ordinary temperature of the air; rectification at boiling temperature over charcoal is altogether unsuitable, owing to the fact that the fusel oil absorbed by the charcoal is again readily dissolved at that temperature. The charcoal to be employed is granulated and passed through a sieve, in order to remove adhering dust. The granulated charcoal is placed in a copper cylinder, fitted at the top and bottom with a perforated plate or disc. This cylinder is connected with the distilling apparatus between the dephlegmator and rectificator in such a manner that the vapours pass through the charcoal. To 100 litres of brandy to be purified, 3 to 5 litres of granulated charcoal are generally required; this can be again employed after having been re-burnt at a bright red heat. Falkmann's apparatus consists of a helm-shaped vessel, *A* (Fig. 537), in which the perforated diaphragms, *b b b*, are placed; upon each diaphragm a layer of charcoal, surmounted with a cover, *c*, is placed. The apparatus is closed with a hollow cover containing a layer of charcoal, *d d*. The vessel, *A*, is surrounded by a cooling apparatus, which in the cut is represented by the cold-water tubes, *f f f*, and the hot-water (which becomes hot by

Fig. 537.



the passage of alcoholic vapours through *A*) tubes, *e e e e;* these serve the purpose of regulating the temperature of the layers of charcoal.

100 litres of Cognac distilled from wine contained, according to Morin (1887)—

Aldehyde	trace
Ethylic alcohol	50·837
Propylic alcohol (normal)	27·170
Isobutylic alcohol	6·520
Amylic alcohol	190·210
Furfurol bases	2·190
Oil of wine	7·610
Acetic acid	trace
Butyric acid	trace
Isobutylglycol	2·190
Glycerine	4·380

Butylic alcohol is absent. The presence of furfurol can be directly shown by adding aniline to the Cognac. It is noteworthy that wine contains amylic alcohol.

Brockhaus has examined by experiments upon himself the action of the most important impurities of potato-spirit: aldehyde, paraldehyde, acetal, propylic-isobutylic and amylic alcohol. 10 drops of aldehyde in 100 grammes of water had a repulsive, and violently burning taste; there was a sensation of burning on the tongue and in the throat, a repulsive after-taste, not to be removed by frequent draughts of water, cough, feeling of suffocation, nausea, pain in the stomach, heat in the head, and palpitation of the heart. These symptoms passed away in about an hour. The effects of 10 drops of aldehyde in wine were rather less unpleasant. From the experiments with amylic alcohol and other constituents of fusel the inference seems justified that the impurities of ordinary spirits play a leading part in the development of drunkard's diseases.

Rabuteau (1878) found on analysing 1 litre potato-fusel—

	c.c.
Isopropylic alcohol	150
Primary propylic alcohol	30
Butylic alcohol, ordinary	50
„ „ normal	65
Secondary amylic alcohol (methyl propyl carbinol)	60
Ordinary amylic alcohol (isobutyl carbinol)	275
Products boiling above 132°, containing amylic alcohol	170
Water	125

Yield of Alcohol.—The quantity of alcohol obtainable from any given substance not only depends on the relative quantity of the alcohol-forming constituents (starch, dextrose, or cane sugar) of the raw material applied for the purpose of distillation, but very largely also on the more or less suitable mode of conducting all the operations of the spirit distillation (mashing, fermentation), in properly constructed apparatus. Leaving out of the question the small quantities of glycerine and succinic acid formed by vinous fermentation, chemistry teaches that—

100 parts of starch			yield 56·78	of alcohol
100	„	cane sugar	„ 53·80	„
100	„	dextrose	„ 51·01	„

Experience shows that the yield of alcohol is in practice less than it should be, promising that every mol. of starch or sugar yields 2 mols. of alcohol; 100 parts of cane sugar do not yield in practice the quantity of alcohol above indicated, viz., 53·8 parts, but only 51·1.

100 kilos. of barley			give	44·64	litres of corn brandy at 50° Tralles			
100	„	barley malt	„	54·96	„	„	„	„
100	„	wheat	„	49·22	„	„	„	„
100	„	rye	„	45·80	„	„	„	„
100	„	potatoes	„	18·32	„	potato spirit	„	„

6 litres (quart or maas) of brandy, from the metrical hundredweight (hectolitre, &c.), is reckoned to yield 6 × 50 = 300 per cent. alcohol; 7 litres, consequently, 350; 8 litres, 400. 8 litres at 48 per cent. Tralles = 384 per cent. alcohol. The number of litres of brandy or spirit multiplied by the alcohol in percentage according to Tralles therefore yield—

1 metrical cwt. of	barley	44·64 × 50 = 2232	per cent.	alcohol		
1	„	„	barley malt	54·96 × 50 = 2748	„	„
1	„	„	wheat	49·22 × 50 = 2461	„	„
1	„	„	rye	45·80 × 50 = 2290	„	„
1	„	„	potatoes	18·32 × 50 = 916	„	„

FLOUR AND BREAD.

Modes of Bread Making.—The preparation of bread aims at the production in the flour obtained by grinding up the cereals of such a chemical and physical condition as will tend to render it most readily masticated by the teeth, and, after having been duly mixed with saliva in the mouth, digested by the juices of the stomach. When flour is mixed with water so as to form a dough, and this mixture dried at the ordinary temperature of the atmosphere, a kind of cake is obtained which contains the starch unaltered and in an insoluble state, so that this kind of cake is very difficult to digest, while, moreover, its taste is so unpleasant as to create no appetite. Again, if the cake is dried at the boiling-point of water, it becomes like a dried starch-paste, which is also very difficult to digest. When this temperature only acts upon the surface of such dough, and does not penetrate into the interior, the resulting cake will be a mixture somewhat similar to ship's biscuit, which may always be considered as a strongly dried dough, and, although it may be preserved for almost any length of time, it is far less digestible than bread. The object of the baking process is to impart to the dough so high a degree of heat as to render the starch soluble, while it is further desired to form a light spongy mass, instead of a brittle or watery paste; the heat should be strong enough to torrify and roast the outer surface of the bread mass to such an extent as to form a deeply coloured crust, whereby not only the taste of the bread is greatly improved, but it can also be kept in good condition for some time. The usual means of rendering dough spongy is by vinous fermentation set up by the addition of a ferment, this being either leaven or yeast; a small portion of the starch of the flour is thus converted into glucose, which is then decomposed, yielding alcohol and carbonic acid gas; the latter is prevented from escaping by the toughness of the dough, which is thereby rendered spongy.

The alcohol is of no consequence whatever. White bread is prepared with wheaten flour and yeast; rye meal, or a mixture of rye meal and wheaten flour, with leaven, yields "black" or rye bread. Heeren found that flour in the state in which it is usually applied for bread baking contains an average of 13 per cent. moisture.

The Details of Bread Baking.—The raw materials in the preparation of bread are flour, water, and a ferment; salt, spices, &c., are also used. The composition of the most important kinds of flour and meals is as follows:—

	a.	*b.*	*c.*	*d.*
Water	15·54	14·60	14·00	11.70
Albumen	1·34	1·56	1·20	1·24
Vegetable glue	1·76	2·92	3·60	3·25
Casein	0·37	0·90	1·34	0·15
Fibrin	5·19	7·36	8·24	14·84
Gluten	3·50	—	—	—
Sugar	2·33	3·46	3·04	2·19
Gum	6·25	4·10	6·33	2·81
Fat	1·07	1·80	2·23	5·67
Starch	63·64	64·28	53·15	58·13
Sand	—	—	6·85	—

a. Wheat flour. *b.* Rye meal. *c.* Barley meal. *d.* Oatmeal.

In addition to these kinds of meal, those derived from Zea-Maïs (Indian corn), beans, peas, &c., are occasionally employed for making bread.

The principal phases of the preparation are :—

The Mixing of the Dough.—The mixing of the flour with water is the first manipulation of the baking process. The object of this operation is first to render dextrine and sugar (owing to the action of the gluten upon the starch, the quantity of sugar becomes increased while the mixing process is going on) and some albuminous substances soluble, and next to mix the solution thus formed thoroughly with the starch and gluten of the flour, and to soak and somewhat dissociate these substances; dry yeast or leaven is at the same time admitted to the bread mass, the former ferment being used when it is intended to make white, the latter when black bread is desired to be made.

By sour dough or leaven is understood that portion of the already fermenting dough which is set apart and kept for the next baking operation; it consists of a mixture of flour and water, in which a portion of the starch is converted, partly into sugar, which is again changed by vinous fermentation, and acetic acid, but chiefly into lactic acid, by a process of fermentation, set up by the peculiar conversion into active ferments of the protein compounds of the flour itself. Leaven, therefore, acts as a fermentation-producing substance in a fresh batch of dough, its action being similar to that of yeast, or of already fermenting wort when added to a freshly made wort. After a length of time the leaven becomes putrid and unfit for use as a ferment. As regards the quantity of leaven to be used with the dough nothing definite can be said, since it depends as much on the degree of sourness of the leaven as on the quality of the bread intended to be made; usually, 4 parts of leaven are added to 100 parts of flour, or to 80 parts of bread 3 parts of leaven. In the case of white bread, 100 parts of flour require 2 parts of dry yeast. The mixing of the flour is effected with lukewarm water, at a temperature of from 21° to 37°.

Kneading.—The thin dough obtained from flour, water, and ferment is dredged over with dry flour, and placed in a warm situation for a time, generally during the night. Fermentation is thus set up by the action of the ferment upon the dextrose of the dough, the carbonic acid developed rendering the dough spongy. The sponge thus prepared is next mixed with more flour, to bring it to the consistency required for the baking, this operation being known as the kneading of the sponge. The method usually employed in these operations is that one-third of the total quantity of flour required for a batch is mixed first with water and ferment, and when this mass has come into full fermentation, the two other thirds of flour are kneaded up along with the sponge, sufficient water being added to form a normal dough. After the kneading operation the dough is again dredged over with some dry flour, and left in a warm situation for the purpose of becoming thoroughly spongy; for this continued fermentation only about half the time is required for the first-mentioned

fermentation. In most bakeries, however, this second fermentation is not proceeded with, but the dough is, immediately after having been kneaded, cut up and shaped into loaves.

By means of the kneading the dough becomes squeezed together, and has, therefore, again to be left in a warm situation for further fermentation, during which it heaves up and increases to double its size. The bulk of the dough increases twofold. When rye bread is made, the dough is frequently moistened on its external surface with lukewarm water, applied by the aid of a brush, in order to prevent cracks in the outer coating of the dough by the evaporation of the water; just before putting the loaves into the oven this brushing over with water is repeated. The water softens the outer surface of the dough, and dissolves some of the dextrine it contains, which substance, after the evaporation of the water from the surface, remains as a glaze upon this kind of bread. When the loaves have risen sufficiently and exhale a peculiar vinous odour, it is time to commence the baking process. Since the bread loses considerably in weight during the baking, the baker must proportion so much dough to each loaf before baking as will yield the legal weight of the baked bread. The weight of dough to be proportioned to a loaf of a certain fixed weight varies according to the size of the loaf; but increases comparatively with decrease therein. The dough generally loses in baking about 25 per cent. of its weight. The smaller the loaf, the more crust in proportion to crumb; and since the crust contains less moisture, and consequently weighs less than the crumb, the loss of weight is proportionately greater in a small than in a large loaf.

The use of machinery in kneading dough is gradually extending, and it will doubtless become general wherever bread is prepared on the large scale.

Baking.—The conversion of the fermented dough into bread is effected by baking in ovens, the common kind of which consists of a round or oval hearth, covered with a

Fig. 538.

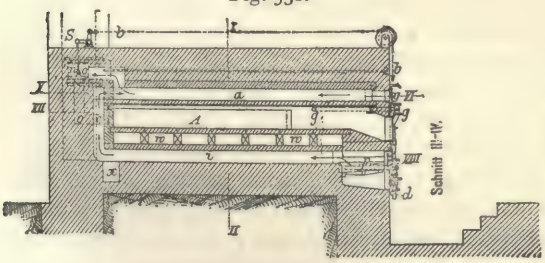
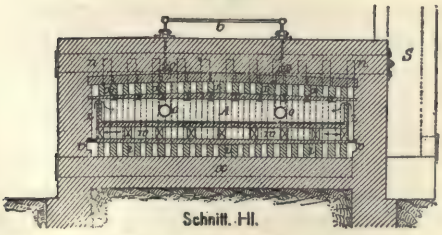


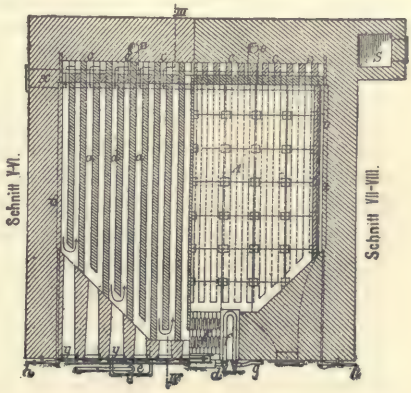
Fig. 539.



Explanation of Terms.

Schnitt III–IV. . . . Section III.–IV.
Schnitt I–II. . . . Section I.–II.

Fig. 540.



Explanation of Terms.

Schnitt V–VI. . . . Section V.–VI.
Schnitt VII–VIII. . Section VII.–VIII.

vault. Far more advantageous are the ovens heated from below, which allow of uninterrupted work with a smaller consumption of fuel and greater cleanliness. In Seidel's oven, *e.g.*, the baking-room, *A* (Figs. 538 to 540), rests on stones forming

parallel channels, whilst the actual hearth is kept at some distance from the side by cubic stones, so as to form the hollow space, *w*. On both sides of the baking-space, *A*, the flues *z* are formed, through which the air heated by the fire-gases passing in the flues *i* rise up and enter the baking-space, *A*. The sole of the space *c* is provided with an opening on both sides, which can be closed by means of the dampers moved by the hand-levers, *h*, and through which the heat, when the firing is completed, can be passed directly into *w* or *A*. To the flues *i*, underneath which there crosses a cleansing flue, *x*, there are joined the flues *c*, which rise up at the rear-wall of the baking-space, and extend to the flues *a*, with the openings for cleansing, *y*. The flues *c* and *a* are so arranged that the heat in each two flues *i* and *c* passes forwards in each one of the flues *a*, turns round backwards in the second of the flues *a*, as shown by arrows on the left hand of Fig. 540, in order to escape into a general flue, *n*, opening into the chimney, *S*. From the water-pan, *e*, a pipe, *d*, leads to the steam generator, *f*. The pipe *g* conveys the steam into the baking-space, *A*, whilst the steam-escape, *o*, which vents into the flue *n*, is regulated by cross-valves and a draught arrangement, *b*.

The temperature of the furnace suitable for baking is 200° to 225°. Before the loaves are introduced into the oven their surface is brushed over with water in order to prevent the crust from bursting in consequence of the too rapid action of a high temperature. The watery vapours with which the oven is gradually filled are necessary in order to convert the starch into dextrine on the surface of the bread, and thus obtain a smooth crust. The time required for baking depends on the size, the shape, and the kind of the loaves. Black bread requires a longer time than white.

Substitutes for Yeast in Baking.—We have seen from the preceding details that the preparation of bread is essentially based upon the fact that by the act of fermentation the gluten of the flour forms a kind of cellular tissue by which the escape of the carbonic acid is prevented, and the bread thus rendered porous and spongy, whereby its digestibility is increased. This quality of the bread is obtained at the cost of a portion of the starch of the flour, which is first converted into starch-sugar, and then by means of fermentation into alcohol and carbonic acid gas; to the expansion of the latter the bread owes its spongy texture. Many attempts have been made for the purpose of effecting the "raising" of the bread, as it is termed, without the use of a ferment, by introducing into the dough some gas- or vapour-producing substance, which would have the same mechanical effect at least as the carbonic acid derived from the fermentation. Although the problem of preparing bread of good quality without the aid of fermentation cannot be said to be quite settled, many proposals have been made in this direction, and some of these deserve notice; we therefore quote the most important. When ammonium sesquicarbonate (the so-called *sal cornu cervi* of pharmacy) is added in small quantity to the dough, it will cause the raising of the same, partly because some acid is always present in the dough, whereby the salt is decomposed and carbonic acid set free, partly because by the heat of the oven the salt is volatilised, and, by assuming the state of vapour, causes the expansion and consequent sponginess of the dough. Liebig recommends the addition of sodium bicarbonate and hydrochloric acid to the dough, the carbonic acid being evolved according to the formula $NaHCO_3 + HCl = NaCl + H_2O + CO_2$, with the formation of common salt, which remains in the dough. The proportions are as follows:—To 100 kilos. of meal for making black bread 1 kilo. of sodium bicarbonate is taken, and 4·25 kilos. of hydrochloric acid of 1·063 sp. gr. (= 9·5° B. = 13 per cent. ClH), yielding 1·75 to 2 kilos. of common salt; the quantity of water to be added amounts to from 79 to 80 litres. From this mixture is obtained 150 kilos. of bread. The proportion of the sodium bicarbonate to the hydrochloric acid is so arranged that 5 grammes of the former are fully saturated by 33 c.c. of the latter, leaving in the bread a faintly acid reaction. The

substance known and sold as Horsford's yeast powder, also recommended by Liebig, is preferable and more readily employed. This powder consists of two separate preparations, viz., the acid powder (acid calcium phosphate with acid magnesium phosphate), the other the alkaline powder (a mixture of 500 grammes of sodium bicarbonate and 443 grammes of potassium chloride). To 100 kilos. of flour, 2·6 kilos. of the acid powder and 1·6 kilo. of the alkali powder are added. During the kneading the following changes occur :—The sodium bicarbonate and potassium chloride are first converted into sodium chloride and potassium bicarbonate, the latter salt being in its turn decomposed by the acid phosphate, whereby carbonic acid is set free. By the use of this baking powder it is possible to make flour into bread within two hours' time, while, moreover, 100 pounds of flour yield 10 to 12 per cent. more bread than with the best method of baking in the usual way. The plan of incorporating pure carbonic acid gas with the dough has been frequently taken up, and successful work has been done in this direction, but the process has its opponents as well as its defenders.

Yield and Composition of Bread.—Flour from various kinds of grain contains in its ordinary air-dry condition from 12 to 16 per cent. of water; by its conversion into bread the flour takes up much more water. 100 lbs. of fine wheaten flour combine with 50 lbs. of water, and give 150 lbs. of bread. The composition of the flour and of the bread is, therefore, as follows :—

	Wheaten Flour.		Wheaten Bread.
Dry Flour	84	...	84
Water originally contained in the flour	16	...	16
Water added for making the dough .	—	...	50
	100	...	150

According to Heeren, 100 lbs. of wheaten flour yield at least 125 to 126 lbs. of bread; 100 lbs. of rye meal, 131 lbs. of bread. Fresh wheaten bread contains 9 per cent. of soluble starch and dextrin, 40 per cent. of unchanged starch, 6·5 per cent. of protein compounds, and from 40 to 45 per cent. of water. As is generally known, newly baked bread possesses a peculiar softness, and is at the same time tough and does not crumble readily : after one or more days' keeping, the bread loses this softness, becomes dry, crumbles readily, and is then called stale or old bread; it is usually supposed that this change is due to a loss of water, but, according to the researches of Boussingault, stale bread contains as much water as fresh bread; the alteration is solely due to a different molecular condition of the bread.

Impurities and Adulterations of Bread.—When the flour intended for the preparation of bread is more or less decayed, the gluten it contains is thereby altered; the carbonic acid evolved during the fermentation of the bread does not render the dough spongy, but it becomes, owing to the altered state of the gluten, a more or less slimy mass, which yields a tough and far less white-coloured bread; in order to counteract this defect, and to impart a good appearance to the bread made from flour which has been damaged by damp, or by having been too closely confined in casks and thereby heated, the bakers in Belgium and Northern France add to the dough a small quantity of copper sulphate, $\frac{1}{15000}$ to $\frac{1}{30000}$; the base of this salt combines with the gluten, forming therewith an insoluble compound, thus rendering the dough tough and white, and capable of taking a large quantity of water. In order to detect the copper sulphate in the bread, a portion of the bread to be operated upon is first dried, then ignited, and the copper separated from the ash by gently washing away the lighter particles, leaving the metallic copper in the shape of small shining spangles.

In England alum was at one time very generally added to flour and bread. But

this fraud, which was always illegal, has been practically suppressed since the appointment of public analysts. In Germany the addition of copper sulphate and of alum is forbidden by the authorities.

MILK, BUTTER, CHEESE.

Milk.—Cows' milk contains, according to the race of the animals, the kind of feeding, &c:—

	Per cent.
Total solids	6·8–17·1
Fat	1·4–7·2
Albuminates	2·2–6·2
Sugar	1·0–5·2
Salts	0·1–1·7

Average samples of total milk taken morning, noon, and evening in three different cow-houses contained, according to Thörner, 1885:—

Time of Milking.	Spec. Grav.		Cream.	Fat.	Total Solids.	Ash.
	Entire Milk.	Skim Milk.				
I.			Vol. per cent.	Per cent.	Per cent.	Per cent.
Morning	1·0306	1·0325	7·0	2·460	10·80	0·57
Noon	1·0304	1·0320	9·0	3·460	12·20	0·58
Evening	1·0311	1·0332	8·0	2·940	11·50	0·60
II.						
Morning	1·0314	1·0329	6·5	2·620	11·37	0·65
Noon	1·0309	1·0339	9·8	3·470	12·09	0·68
Evening	1·0303	1·0317	8·0	3·230	11·74	0·75
III.						
Morning	1·0294	1·0324	11·0	3·470	11·80	0·74
Noon	1·0289	1·0326	11·5	4·004	12·15	0·66
Evening	1·0302	1·0324	13·5	4·630	12·91	0·65

Lot I. consisted of the milk of twenty-five cows, each fed daily with 10 to 12½ kilos. brewery grains, 1 kilo. of a cattle-food (containing 14 per cent. protein and 38 per cent. of non-nitrogenous extractive) and green food, with hay and straw as required.

Lot. II. comprised the milk of thirty-two cows, fed on 80 litres rye-vinasses and 6 kilos. of hay.

Lot III. was obtained from twelve cows, half pasturage and half stall-fed. The latter consisted of red clover with Italian rye-grass and 0·25 kilo. of cotton-seed cake and 1 kilo. of crushed rye.

The composition is hence very variable.*

If we subtract the fat from the dry substance we obtain a figure which varies but little.

Milk is a mixture of several insoluble, very minutely divided, emulsified substances, suspended in a watery liquid. The specific gravity of milk varies from 1·030 to 1·045. Under the microscope it becomes evident that the white colour of milk is due to the so-called milk globules—small globular bodies of a yellow colour, with a more deeply coloured circumference, and exhibiting a pearly gloss. It was formerly believed that these globules consisted of an exterior envelope filled with butter, but the recent researches of Drs. Von Baumhauer and F. Knapp have proved these opinions to be erroneous. When milk is left standing these globules rise to the surface and form cream, below which remains a blue transparent fluid containing the sugar of milk, salts, and caseine, the latter in the form of caseine-soda. When milk is kept for some

* Compare Wanklyn's treatise on the Analysis of Milk. London: Kegan Paul, Trench, Trübner & Co.

time, a portion of the lactose (sugar of milk) is decomposed and converted into lactic acid by the aid of the caseine, which acts as a ferment. In its turn the lactic acid decomposes the caseine-soda, whereby the caseine is set free and separated as an insoluble substance; this action takes place in the coagulation of milk. The whole of the lactose or sugar of milk becomes converted into lactic acid by long keeping.

Lactic acid ($C_3H_6O_3$) is also formed by the fermentation of starch, cane sugar, and glucose, under the influence of caseine and a ferment. This acid is met with in sauerkraut (a favourite dish of the Germans, being a well-preserved mixture of white and savoy cabbages cut into shreds, and packed in casks along with salt, coarse pepper, and some water) and in other pickles, in beer, and in nearly all animal liquids. Lactic acid is also present in some of the fluids of the tan-yard tanks; in the sour water of starch works where starch is prepared by the old methods; in the bran baths of dye works; and is constantly met with in the residual liquids of corn spirit distillation. When lactic acid is heated with sulphuric acid and peroxide of manganese, aldehyde is formed, which is used in the preparation of aniline green and of hydrate of chloral.

The coagulation of fresh milk is effected by the use of rennet, which is prepared from the stomach of a calf, well washed and stretched out on a wooden frame, then dried either in the sun or near a fire. The substance thus prepared was formerly soaked in vinegar, but experience has proved this to be unnecessary. When required, a small piece is cut off and steeped in warm water, and the liquid added to the milk, previously heated to from 30° to 35°. The milk is hereby coagulated, even in large quantity, in about two hours; 1 part of rennet is sufficient for the purpose of coagulating 1800 parts of milk. The mode of action of rennet is not well understood, but it does not consist, as was formerly believed, in the instantaneous conversion of a portion of the lactose present in milk into lactic acid, since experiments have shown that rennet coagulates milk which exhibits an alkaline reaction.

Whey.—By the term whey is understood the fluid in which the coagulated caseine of milk floats, and which may be obtained either by decantation or filtration. The whey of sour milk contains very little lactose and a large quantity of lactic acid (sour whey); while sweet whey, obtained by coagulating milk with rennet, contains all the lactose. Sweet whey containing 3 to 4 per mille of a proteine compound (termed lacto-proteine by Millon and Commaille) is evaporated to some extent in Switzerland, with the view of obtaining the sugar of milk in a crystalline state. The substance thus obtained is purified by recrystallisation.

Lactose (*Sugar of Milk*), $C_{12}H_{22}O_{11} + H_2O$, does not possess a very sweet taste, and feels sandy in the mouth. It is soluble in 6 parts of cold and 2 parts of hot water. It is not capable of alcoholic, but only of lactic acid fermentation. By the action of dilute acids sugar of milk is converted into galactose, a kind of sugar similar to grape sugar, and is then capable of alcoholic fermentation. Industrially, sugar of milk is sometimes employed for the purpose of reducing a silver solution to the metallic state, as in the case of looking-glass making. 100 parts of the commercial sugar of milk from Switzerland (*a*), and from Giesmannsdorf in Silesia (*b*), were found to consist (1868) of:—

	a.		*b.*
Salts	0·03	...	0·16
Insoluble matter	0·03	...	0·05
Foreign organic substances	1·14	...	1·29
Sugar of milk	98·80	...	98·50
	100·00	...	100·00

Uses of Milk.—Milk is used as food and for the preparation of butter and cheese, for clarifying wine in order to render it less deep-coloured and, if turbid, quite clear.

More recently milk has been largely sold in the so-called condensed state, by which is understood milk evaporated *in vacuo*, after the addition of sugar, to the consistency of thick honey. This mode of preserving milk was first employed by the Anglo-Swiss Condensed Milk Company at Cham, Canton Zug, Switzerland, and is now carried on in various parts of the Continent and in the United States, and also in England, in Surrey and Buckinghamshire.

The average composition of condensed milk, according to Soxhlet, is—

	I.		II.
Water	26·88	...	24·70
Salts	2·26	...	2·11
Fat	8·67	...	6·02
Albumen	11·07	...	9·77
Sugar	51·12	...	57·40

Kefyr is obtained by a peculiar fermentation of cows' milk set up by certain fungi. The fermentation of mares' milk yields *koumiss*. Three samples of koumiss had the following composition :—

	I		II.		III.
Water	91·87	...	92·38	...	92·42
Alcohol	3·29	...	3·26	...	3·29
Fat	1·17	...	1·14	...	1·20
Caseine	0·80	...	0·85	...	0·79
Albumen	0·15	...	0·32	...	0·32
Lacto-proteine and peptone	1·04	...	0·59	...	0·76
Lactic acid	0·96	...	1·03	...	1·00
Sugar	0·39	...	0·09	...	—
Ash, soluble	0·10	...	0·12	...	0·12
„ insoluble	0·23	...	0·22	...	0·23

Butter.—This substance is prepared as follows :—Milk of good quality is placed in a rather cool cellar or other locality for the purpose of causing the cream to separate. The cream is poured into a clean stoneware or glass vessel kept for the purpose, and left until by constant stirring it has become thick and sour; it is then put into a churn, by the action of which the solid fat globules are separated from the thick fluid in which the caseine with a small quantity of butter remains suspended. Butter, being specifically lighter than water, should, it might be thought, separate very readily from a liquid which contains in solution various substances which are heavier; but the fact is that caseine renders the separation of butter from cream difficult even when the cream is sweet and not thick; when, on the other hand, milk coagulates before the cream is separated, the butter is lost. Two methods have been devised for the purpose of obtaining all the butter contained in milk. Gussander, a Swedish agriculturist, has proposed that the separation of cream should be rendered more rapid, and always completed before the milk becomes sour, while Trommer prevents the souring of the milk by the addition of some soda.

The liquid from which the butter is separated is known as churn-milk or butter-milk; it contains 0·24 per cent. butter, 3·82 per cent. casein, 90·80 per cent. water, 5·14 per cent. sugar of milk and salts. Lactic acid is present in the water. 18 parts of milk yield on an average 1 part of butter, which in fresh condition consists of—

	I.		II.		III		IV.
Butter fat	94·4	...	93·0	...	87·5	...	78·5
Caseine, sugar of milk Extractive matter	0·3	...	0·3	...	1·0	...	0·3
Water	5·3	...	6·7	...	11·5	...	21·2

Owing to the presence of water and caseine, butter after some time becomes rancid. It is salted in order to prevent this rancidity as much as possible, the salt being thoroughly mixed with the butter by kneading. To 1 kilo. of butter 30 grammes of

salt are required. According to Dr. Wagner, butter in England is salted with a mixture of 4 parts of common salt, 1 part of saltpetre, and 1 part of sugar. In Scotland, France, and Southern and Western Germany, butter is not salted at all, and is therefore only made and sold in comparatively small quantities at a time. Salt butter is termed in Scotland pounded butter.

By melting butter until the first turbid liquid has become clear and oily, water and caseine are eliminated, and, settling to the bottom of the vessel, the supernatant fat may be put into another vessel, and will, after cooling, keep sweet without salt for any length of time. Butter is often artificially coloured by the aid of either annatto, turmeric, or infusion of calendula flowers.

Chemical Nature of Butter.—Butter consists of a mixture of neutral fats (glycerides) which on being saponified yield several fatty acids, among which the non-volatile are—Palmitinic acid ($C_{16}H_{32}O_2$) and butyroleic acid ($C_{12}H_{30}O_2$). The volatile are—Butyric acid* ($C_4H_8O_2$), capronic acid ($C_6H_{12}O_2$), caprylic acid ($C_8H_{18}O_2$), and caprinic acid ($C_{10}H_{20}O_2$). The last four constitute in the shape of glycerides the butyrin or special fat of butter, and impart to that substance its peculiar odour and flavour.

Schmitt examined two samples of cow-butter with the following results:—

	I.		II.
Melting-point	36·5°	...	36·5°
Fat	86·250	...	86·50
Water	9·800	...	10·54
Caseine	2·225	...	1·42
Ash	0·100	...	0·85
Solid fatty acids, insoluble in water	88·570	...	89·15
Volatile acids, soluble in water	4·452	...	4·45
Melting-point of solid fatty acids	39·8°	...	40·0°

Composition of Butter Fats:—

Butyrine [$C_3H_5(O.C_4H_7O)_3$]	5 per cent.
Oleine [$C_3H_5(O.C_{18}H_{33}O)_3$]	60 „
Margarine (tristearine and tripalmitine)	35 „

Rancid butter contains free butyric acid, 0·02 gramme of which per kilo. is sufficient to spoil the taste.

Artificial Butter (*Margarine and Oleomargarine*) is now manufactured on the large scale. At first the process consisted in softening tallow by a gentle heat and freeing it by pressure from the excess of stearine, thus producing a softer mixture of oleine and palmitine. Such mixtures were formerly called margarine, under which name and that of "oleomargarine" artificial butter is now legally sold, according to the law for the prevention of fraud. The want of the smell and taste of genuine butter is in part overcome by a treatment similar to that which true butter undergoes in churning.

This manufacture was first established by Mège-Mouriès at Vincennes in 1869. The tallow, washed in water and comminuted, is cautiously melted. The clear, yellow liquid deposits on standing all membranes, &c. The liquid is let off into large wooden cisterns and conveyed into a room of the temperature of 20°, where it cools slowly. In from twelve to twenty-four hours sufficient stearine has separated out in a granular-crystalline form; the cisterns are removed to the press-room, where at an air temperature of 30° the soft fatty masses, wrapped in press-cloths, are exposed to a gradually increasing pressure. The liquid oily fat drains off; the press-cakes consist of white stearine, which is used in the manufacture of soap and of candles. The expressed oil, consisting of a hot saturated solution of stearine and palmitine in oleine, is cooled

* This acid is formed, not only by the saponification of butter, but is also met with in secreted perspiration and the juices of the stomach, and results from the fermentation and decay of sugar (in weak solutions), starch, fibrine, caseine, &c.

down to 20°, and then worked up in butter kegs with sour milk and a little of the colouring matter of annatto. After ten to fifteen minutes the mixture becomes uniform, and is emptied out through an opening in the bottom into a vessel, where it is stirred up with powdered ice in order to prevent the fat from separating out in a granular form. In from two to three hours the mass is taken out and divided on tables with slightly sloping tops, so that the ice may melt away. Lastly, the butter is salted by working in 2 to 3 per cent. of common salt. Or to 200 kilos. of solid fat there is added the stomach of a sheep or a swine finely mixed up and so much calcium phosphate and hydrochloric acid as to form an artificial gastric juice, and heated to 20°–50°. In an hour there rises to the surface a yellow liquid of a butter-like smell. This is drawn off and mixed with $\frac{1}{4}$ per cent. common salt at 45°, which eliminates a small quantity of a ferment. When clear the mass is allowed to crystallise at 25°, the liquid part is pressed out and mixed in the butter keg with 12 to 20 per cent. of sugar, to which $\frac{1}{1000}$ sodium bicarbonate has been added. After churning for half an hour it is allowed to cool and solidify.; all the milk is pressed out of the mass by passing it under rollers, and it is moulded for sale. As a matter of course, artificial butter should be sold only as such. When carefully prepared it is less liable to turn rancid in hot climates than is natural butter.

Cheese.—Cheese is prepared from caseine. It is made either from skimmed or unskimmed milk. In the former case a lean, dry cheese is obtained; in the latter a fat cheese, such as Cheshire, Cheddar, American, and the bulk of Holland cheeses. Lean cheese is made in Germany by pouring the skimmed and already sour milk upon a cloth, through the pores of which the whey passes, while the caseine remains on its surface as a pasty mass, which is put by hand into the cheese-moulds, these being next exposed to air.

Fat cheese is made of sweet milk just drawn from the cows, the milk being coagulated by rennet after having been heated to 30° to 40°. The gelatinous mass thus obtained is broken up and pressed by hand, and the whey gradually removed by the aid of wooden ladles. The caseine, having been freed from whey, is next well kneaded with some common salt, and then put into wooden moulds with two or three small holes at the bottom for the purpose of allowing the whey to flow off when the cheese is pressed. The newly made cheese is usually dipped every alternate day in warmed whey, next wiped dry, put into the mould again, and pressed. When the crust has sufficiently formed and the cheese become so hard as to admit of being handled, some salt is rubbed into its surface, and it is then placed in a cool well-aired room upon a shelf to dry and become, as it is termed, ripe. The vesicular appearance of some kinds of cheese (the Gruyère cheese exhibits this in a high degree) is indirectly due to the incomplete removal of the whey, the sugar contained becoming, during the ripening, converted into alcohol and carbonic acid, which by its expansion while escaping produces the vesicular texture. Dutch cheese does not exhibit this appearance, on account of being strongly pressed and containing much salt, by which the fermentation of the sugar of milk in the cheese is prevented. The quality of the cheese depends to some extent npon the temperature of the room in which it ripens. At Allgäu 1 cwt. of Swiss cheese of the first quality is produced from 600 litres of milk, while for the second quality 720 to 750 litres of milk are taken for the same weight. The theory of cheese formation is not well known, but it appears that fermentation plays an important part in it. W. Hallier has proved that freshly made cheese is filled with ferment nuclei (*Kernhefe*).

Cheese cannot be formed without this ferment, and by the addition of suitable ferments the duration of the cheese-ripening process and the quality of the cheese may be to some extent regulated at will. By exposure to air cheese undergoes changes which may be best observed in skimmed-milk cheese. When new or young its colour is white. By being kept so that it does not dry, it turns yellow and often

becomes transparent, waxy and then exhibits the peculiar odour of cheese. When cheese gets very old it becomes a soft and pasty mass, this change commencing at the outside and progressing towards the interior. The waxiness of cheese is due to an evolution of either ammonia or acid. Mild cheese usually exhibits an acid reaction, while strong cheese is ammoniacal. Chemically speaking, skimmed-milk cheese is a compound of caseine with ammonia or ammonia bases—amylamine, for instance. The so-called dry cheeses, green Swiss cheese, contain an infusion of herbs, *Melilotus*, &c., with volatile fatty acids, valerianic, capric, and caproic acids, and indifferent substances, leucin, &c. The composition of sweet milk cheese (*a*) and of sour skim-milk cheese (*b*) is exhibited by the following table :—

	a.		*b.*
Water	36·0	...	44·0
Caseine	29·0	...	45·0
Fatty matter	30·5	...	6·0
Ash	4·5	...	5·0
	100·0	...	100·0

The results of the researches of Payen on cheese are quoted below in 100 parts for the following kinds :—(1) Brie, (2) Camembert, (3) Roquefort, (4) Double cream, (5) Old Neufchatel, (6) New Neufchatel, (7) Cheshire, (8) Gruyère, (9) Ordinary Dutch, (10) Parmesan.

	I.				
	1.	2.	3.	4.	5.
Water	45·20	51·90	34·50	9·50	34·50
Nitrogenous matter	18·50	18·90	26·50	18·40	13·00
Nitrogen	2·93	3·00	4·21	2·92	3·31
Fatty matters	25·70	21·00	30·10	59·90	41·90
Salts	5·60	4·70	5·00	6·50	3·60
Non-nitrogenous organic matter and loss	5·00	4·50	3·90	5·70	7·00
	II.				
	6.	7.	8.	9.	10.
Water	36.60	35·90	40·00	36·10	27·60
Nitrogenous matter	8·00	26·00	31·50	29·40	44·10
Nitrogen	1·27	4·13	5·00	4·80	7·00
Fatty matters	40·70	26·30	24·00	27·50	16·00
Salts	0·50	4·20	3·00	0·90	5·70
Non-nitrogenous organic matter and loss	14·20	7·60	1·50	6·10	6·60

The varieties mentioned under I. exhibit an alkaline reaction, and contain, with ammonia, cryptogamic plants, or, as it is termed, are mouldy. The varieties under II., so-called boiled, strongly pressed, and salted cheese, exhibit an acid reaction, as also does freshly prepared caseine. A portion of the fat contained in the cheese is even from the first decomposed into glycerine and fatty acids.

Emmenthaler (*a*) and Backstein (*b*) cheese are composed, according to Lindt's researches (1868), as follows :—

	a.		*b.*	
Water	37·4	36·7	45·2	35·8
Fatty matters	30·6	30·5	28·2	37·4
Caseine	28·5	29·0	23·2	24·4
Salts	3·5	3·8	3·4	2·4
	100·0	100·0	100·0	100·0

The results of E. Hörnig's recent analyses (1869) of different kinds of cheese are:—

	1.	2.	3.	4.	5.	6.	7.	8.
Water . . .	38·66	56·60	51·21	57·64	36·72	34·08	59·28	49·34
Fatty matters .	20·14	17·05	9·16	20·31	33·69	28·04	10·44	20·63
Caseine . . .	34·90	18·76	33·60	18·51	25·67	23·28	24·09	24·26
Salts . . .	6·17	6·78	6·01	3·51	3·71	5·58	6·17	5·45
Loss . . .	0·13	0·81	0·02	0·04	0·71	0·02	0·02	0·32
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

No. 1 was Dutch cheese; 2 and 3, Ramadoux cheese, made in Bavaria; 4, Neufchatel cheese; 5, Gorgonzola cheese; 6, Bringen or Liptau cheese, from the Zyps Comität, Hungary; 7, Schwarzenberg cheese; 8, Limburg cheese, made in the environs of Dolnain-Limburg, in Belgium.

Every rennet contains, according to Benecke, the hay bacillus, *Bacillus subtilis*, which is also present in ripening cheese. There is also a bacterium, which splits off butyric acid from the albuminoids, and this, if it is formed in unusual quantities, gives the cheese a bad flavour.

Loose, fat cheese is digested in from four to ten hours; lean cheese is more difficult of digestion.

Freshly made caseine mixed with lime is used as a kind of cement. Caseine is also used in calico-printing as a mordant, under the name of "lactarine"; and a solution of caseine in borax is used instead of glue. In the seeds of the leguminous plants, peas, beans, lentils, &c., a nitrogenous substance is met with which is soluble in water and precipitable therefrom by weak acids; this material is very similar to caseine, and, according to M. J. Itiers's accounts, in China peas and beans are boiled with water and strained, and to the liquid thus obtained some solution of gypsum is added, whereby the vegetable caseine (legumine) is coagulated, and the coagulum thus obtained is treated as that of milk, obtained by the addition of rennet to the latter. The mass so obtained gradually becomes like cheese in all respects.

MEAT.

What is commonly known as meat is the muscular substance of the slaughtered animals, together with more or less fat and bone.

Muscular tissue is histologically composed of a variety of complex tissues and fluids, the basis of which is animal fibre or fibrin, an organised proteine compound. The muscular fibre held together by cellular tissue forms the muscle, fat being deposited in the cellular tissue and in cells peculiarly constructed for that purpose. Blood-vessels, lymph-vessels, nerves, and other organised tissues are dispersed through the muscles, and serve a variety of physiological purposes. The muscular tissue is impregnated with a proteine fluid in which a variety of other substances are met with, as kreatinin, hypoxanthin, kreatin, inosite or muscular sugar, lactic acid, inosinic acid, extractive matter, and inorganic salts—among these being potassium chloride and magnesium phosphate.

Constituents of Meat.—The average results of a great number of researches recently made on the large scale concerning the quantity of water contained in the meat of fattened or half- or non-fattened animals are the following:—

	Lamb.	Sheep.	Bullock.	Pig.
In the non-fattened meat .	62	58	—	56
„ half-fattened meat .	—	50	54	—
„ fully fattened meat .	49	40	46	39
„ fat meat . . .	—	33	—	—

Hence it appears that with an increase of fat the quantity of water present in meat decreases, a portion being replaced by fat. Well-fed and fattened meat contains for equal weights about 40 per cent. more dry animal matter than non-fattened meat, while in highly fattened meat it may amount to 60 per cent.

The difference in nutritive value of the meat of well-fattened bullocks as compared with that of non-fattened is exhibited in the following percentage results obtained by Breunlin:—

	Fattened.		Non-fattened.
Water	38·97	...	59·68
Ash	1·51	...	1·44
Fat	23·87	...	8·07
Muscle	35·65	...	30·81
	100·00	...	100·00

1000 grammes contain—

	Muscular Meat.		Fat.		Ash.		Water.
Meat from fattened bullocks	356	...	239	...	15	...	390
Meat from non-fattened bullocks	308	...	81	...	14	...	597
Difference	+48	...	+158	...	+1	...	−207

Consequently, the meat of fattened bullocks contains in 1000 parts 207 more of solid nutritive matter than the meat of the same in unfattened condition.

The Cooking of Meat.—Meat is either roasted or boiled. By boiling, meat is very essentially altered in composition according to the time it is boiled, and the quantity of water used to boil it in. The fluid in which meat has been boiled contains soluble alkaline phosphates, salts of lactic and inosinic acids, magnesium phosphate, and a trace of calcium phosphate. In order to be of the highest nutritive value, meat should retain all its soluble constituents; hence, boiled meat loses much in nutritive power. The albumen contained in meat is lost by boiling according to the usual plan. Meat intended to be boiled should be immersed in boiling water to which some salt has been added, the meat being put in while the water boils violently, whereby so great a heat is at once imparted to the outer portions of the meat as to coagulate the albumen, which then acts as an impermeable layer, retaining the juices in the meat. Liebig's directions for making good broth are the following:—Lean meat is minced, mixed with distilled water, to which a few drops of hydrochloric acid and common salt are added. After having been digested in the cold for about an hour, the liquid is strained through a sieve, and upon the residue some distilled water is again poured so as to extract all soluble matter. In this way an excellent and highly nutritive cold solution of extract of meat is obtained; this may be drunk without being heated, and contains albumen in solution, which is coagulated by heating. 100 parts of beef yield an extract containing 2·95 parts of albumen and 3·05 parts of other constituents of meat not coagulable by heat. Chevreul obtained from 500 grammes of beef containing 77 per cent. water, 27·25 grammes of extract, in which were 3·25 grammes fat; deducting these, there remain 4·8 per cent. extract. The bulk of this fluid extract was 1·25 litre, the weight 1004·09 grammes, and it contained—

Water		991·30
Organic matter	Soluble in alcohol	0·44
	Insoluble in alcohol	3·12
Alkaline salts		8·67
Earthy phosphates		0·56
		1004·09

Broth made from beef contains only 3 parts of meat substance, inclusive of glue and fat.

Under the best conditions, 1 kilo. of beef yields—

Soluble in cold water	60	Coagulated albumen	29·5
		Albumen in solution	30·5
Insoluble in cold water	170	Glue-yielding substance	6·0
		Fibrous matter	164·0
Fat	20		
Water	750		

The Boiling of Meat.—We have already stated that the meat intended to be boiled should be immersed in boiling water and the fluid kept boiling for a few minutes, so much cold water being next added as will reduce the temperature of the liquid to 70° or 74°. At that heat the liquid should be kept for some hours to produce a very savoury, sweet, succulent piece of boiled meat. If, however, it is desired to make a strong broth, lean meat is first minced, next well exhausted with cold water, and then slowly heated—best on a water bath—and just allowed to come to the boil over a slow fire. The liquid is strained from the solid meat, and the latter put into a clean cloth and well pressed. The residue is fit only for the making of manure. The broth may be coloured with caramel if desired. Broth so made contains all the soluble constituents of meat, and exhibits an acid reaction owing to the free lactic and inosinic acids. Broth does not owe its good properties to the gelatine it contains, this substance being present in very small quantities, while the so-called *bouillon tablettes* obtained from bones are altogether unfit for food. These *tablettes* should not be confused with solid-meat extract cakes of Russian make, which contain, according to Reichardt (1869)—

Water driven off at 100°	15·13	per cent.
Ash	4·75	„
Fat	0·22	„
Nitrogen	10·57	„
Substance soluble in alcohol at 80 per cent.	38·09	„

When broth is boiled for a long time it becomes deep-coloured and assumes the very agreeable flavour of roast meat. Evaporated upon a water-bath it yields a pasty, deep brown-coloured mass, 18·27 grammes of which yield, with 1 lb. of hot water and the addition of some salt, a very strong and excellent soup. 32 lbs. of bones, with the adhering scraps of lean meat, yield 1 lb. of this extract. Extract of meat, as generally met with, is now made in South America by several firms, at Fray-Bentos, Uruguay, Gualeguaychu (Entre Rios). 1 kilo. of this extract contains all the soluble portion of 34 kilos. of meat without bones, or 45 kilos. of average butchers' meat. Australian extract of beef (the American extract is of mutton and beef mixed, manufactured by R. Tooth) is largely imported into Europe. The chief test for the purity of the extract of meat is its solubility in alcohol at 80 per cent., next the quantity of moisture it contains, and the absence of albumen and fat. At least 60 per cent. of the extract should be soluble in alcohol. The quantity of water amounts to about 16 per cent., the nitrogen to 10 per cent., and the ash to 18 to 22 per cent., consisting essentially of calcium and magnesium phosphates, and chlorides of the alkalies, among which potassium chloride predominates.

Preservation of Meat.—Among the many methods employed for the preservation of meat, that by complete exclusion of air ranks foremost. Appert's plan of packing meat in tin canisters, from which the air is completely exhausted, is generally the following :—The meat, or very concentrated soups, game, &c., is put into tin canisters, which are thoroughly filled. A lid is then soldered on, in which a small hole is made for the purpose of entirely filling any interstices with gravy. This having been done, the small hole is soldered over, after which the canisters are placed in a cauldron filled

with brine and boiled therein for a half to four hours, according to the size of the canisters. When any of them is not well soldered, there will issue from the leakage smaller or larger vesicles of air and vapour, and where such is the case hot solder is applied on the spot. By this boiling the albuminous substances are coagulated and converted into a less readily putrescible modification. The oxygen of the air contained in the canisters is partly converted into carbonic acid, partly deozonised, and thus rendered ineffective for the production of putrescence. After having been submitted to the action of boiling heat for some time, the canisters are placed in a room heated to 30°, and left there in order to test whether putrefaction can set in, manifested by the bulging outward of the top cover, which, if the operation has been thoroughly successful, is usually somewhat concave in consequence of a vacuum having been formed inside the tin. After having been thus tested for several days, the canisters may be considered sound, and will keep for an indefinite period. Dr. Redwood's method of preserving meat under a layer of paraffin, and Shaler's plan of preserving meat in dry carbonic acid gas at 0°, are in principle the same as Appert's method.

Preservation of Meat by Withdrawal of Water.—Meat may be preserved by drying it or salting it, both methods being based upon the withdrawing of the water. Although drying is the best method of preserving meat, it is an operation attended with very great difficulty. The natives of North and South America cure meat by cutting it into thin strips, removing the fat, and rubbing Indian-corn meal on the surface. Thus prepared, the meat is exposed to the heat of the sun, and dries rapidly forming a flexible, non-putrescent mass, which in North America is termed *Pemmican*, in South America *Tassajo*, and in South Africa *Biltongue*. 100 parts of beef, which is, after drying, rolled up so as to form a compact mass, yield 26 parts of tassajo. The drying of meat is in Europe never effected on a large scale, partly on account of the low temperature, partly on account of the necessity of cutting the meat into pieces, rendering it in many instances unfit for culinary purposes.

Many preparations of flour and meat extract have been introduced at different times under the name of meat biscuit, first made in 1850 by Gail Bordon at Galveston, Texas, U.S., and greatly improved upon by C. Thiel at Darmstadt. The latter minces fresh lean meat, next exhausts it with water, and uses the liquid obtained for mixing with the flour instead of water. The large biscuit manufacturing firms in England, especially Huntley & Palmer at Reading, prepare patent meat biscuits or wafers, made with Liebig's extract of meat and Hassall's flour of meat. On the Continent, E. Jacobsen at Berlin prepares a similar biscuit, more especially with the view of preparing soup. To the mixtures of animal and vegetable matter prepared so as to be suitable for keeping for a length of time belong the pea-sausages, first made by Grüneberg at Berlin, and largely used as an excellent food for the German armies during the Franco-Prussian war.

Salting Meat.—This method of preserving meat, based upon the principle of withdrawing water, has been used from time immemorial. The salt, while penetrating into the meat and thereby hardening it, displaces the water and aids the preservation of the substance. The freshly slaughtered meat is first rubbed with coarse salt, and then left in a cask with salt for some days. It is next pressed and put into another cask, the wood of which has been previously soaked with brine. Some salt is then added, and lastly the brine, which had been obtained by pressing the meat, is poured over it, and the lid of the cask put on. Frequently some potassium nitrate and sugar are added, as well on account of the antiseptic property of these substances as for imparting a bright red colour to the meat.

Salt, however, not only withdraws water from the meat, but also, as has been proved by Dr. Liebig's researches, some of the very best and essential portion of the juices of

the meat, including albumen, lactic and phosphoric acids, magnesia, potash, kreatin, and kreatinin. Hence it is clear that unless these substances are in some way or other added to the salted meat, its use as food for a lengthened period cannot fail to become injurious to the system, and it is surmised that scurvy is due to this condition of salt meat. Liebig has suggested that meat, instead of being treated with dry salt, should be salted with a strong brine made up of common salt, Chili saltpetre, potassium chloride, and extract of meat. The salt to be used for making this brine should be previously purified by the application of a solution of sodium phosphate, whereby lime and magnesia are precipitated. Cirio's method of meat preservation, which was exhibited in 1867 at the Paris Exhibition, consists in placing the meat *in vacuo* and then forcing brine into it. By this process the nutritive value of meat is much impaired, owing to the loss of the juices.

Smoking or Curing Meat.—The *rationale* of this process and the preservative action of the smoke have not been scientifically elucidated. In the first place, the heat of the smoke dries the meat, while, further, smoke contains a creosote, which, according to the more recent researches of Hlasiwetz, Gorup-Besanez, Marasse, and others, essentially consists of a mixture of $C_7H_8O_2$, $C_8H_{10}O_2$, and $C_9H_{12}O_2$. This creosote possesses the property of coagulating the albuminous substances of meat, and once coagulated, and thereby rendered insoluble, these substances are not capable of decay, or only so after a very great lapse of time. Smoke, moreover, contains some pyroligneous acid and other creosote-like substances (oxyphenic and carbolic acids), which undoubtedly play some part in the preservative action.

Vinegar is an excellent preservative of meat, especially in hot summer weather. Abroad, meat is frequently put into a clean linen cloth which is thoroughly soaked with vinegar, some salt also being sprinkled on the cloth. Meat kept for a few days in this manner is very tender and readily digested. It is very probable that vinegar might be advantageously employed on the large scale for the preservation of meat, together with complete exclusion of air. In order to prevent the vinegar extracting the juices of the meat, the latter should be exposed to the action of the vapours of strong vinegar.

Lamy more recently, and Braconnot, Robert, and De Dombasle nearly half a century ago, proposed to preserve meat by the aid of sulphurous acid gas, pieces of meat weighing from 2 to 3 kilos. being exposed to the action of this gas for ten minutes, while larger pieces, of 10 kilos. or more, are exposed to the action of the gas for twenty to twenty-five minutes. After having been exposed to fresh air for some minutes for the purpose of getting rid of the excess of the gas, the meat is coated, with a brush, with a solution of albumen in a decoction of marsh-mallow root to which some molasses have been added. Very recently meat has been preserved by first drying it in a current of hot air and next coating it with a film of caoutchouc or gutta-percha, by immersing the meat in a solution of these substances in chloroform or sulphide of carbon. It is very generally known that a temperature below freezing-point is a most perfect protection against decay of animal matter; hence ice is largely used for the preservation of fish in summer time. Meat, as well as game and poultry, are best preserved in hot weather in ice-pits. In no country in the world is so much use made of this mode of preserving meat and vegetables as in Russia, where the very severe winter is turned to good account for preserving all kinds of animal food; in fact, oxen, sheep, hogs, deer, and all kinds of game and poultry are brought to market in a frozen condition, and may be kept so for any length of time without impairing the goodness or taste after cooking. At St. Petersburg large stores of frozen animal food and game brought from distances of hundreds of miles are kept throughout the winter. At the Dornburg, near Hadamar (Province of Nassau, Prussia), a natural permanent ice store exists, wherein perishable food is kept stored in large quantity.

The artificial production of ice by means of Carré's machine is employed in New South Wales for the freezing of meat, which is next packed in ice ready for transport.

It must be added that the process of smoking meat has some resemblance to a tanning process, whereby its digestibility is naturally diminished. On the other hand, the digestibility of meat can be improved by rubbing it with the juice of *Carica papaya*.*

NUTRITION.

The blood circulating in the living animal body consists of a clear liquid, containing substances capable of forming albumen and fibrine, and numerous microscopic corpuscles, especially hæmoglobin. This hæmoglobin takes up in the lungs the oxygen of the inhaled air, and assumes in consequence a bright red colour. The bright red arterial blood gives off this oxygen whilst circulating through the body, and the hæmoglobin of the blood-corpuscles absorbs carbon dioxide in its place, which the venous blood, rendered thereby darker, exchanges again for oxygen in the lungs. A man inhales at every breath about 0·5 litre of air, and consumes daily 750 grammes oxygen, giving off 320 grammes watery vapour and 900 grammes carbon dioxide.

The food is moistened in the mouth by the saliva secreted by three glands, which converts starch into dextrine and sugar. The food encounters in the stomach the strongly acid gastric juice containing free hydrochloric acid and pepsine. This agent prepares the proteine matters in the food for reception into the blood. In the bowels the digestion is completed by the alkaline pancreatic secretion and the gall, when the substances suitable for the formation of blood are taken up by the lymphatic vessels and conveyed into the veins.

By the inspiration of oxygen the parts of the body are oxydised and conveyed away by the blood, the carbon dioxide being eliminated in the lungs, and the urea, $CO(NH_2)_2$, formed from the proteine substances, in the kidneys. These losses must be compensated by the blood, to which fresh matter must be conveyed by taking food.

Nutrition has therefore two distinct tasks to fulfil—viz., (1) the formation and preservation of the body; (2) supply and utilisation of energy for the power of the entire body and its organs—*i.e.*, the production of heat, mechanical work, and electricity. The first duty is chiefly assigned to the albuminoids; in the production of power all the organic matters are concerned according to the sum of the tension forces contained in them and liberated by the metabolism in the body. The non-nitrogenous substances, which only play a subordinate part in building up the organs, but possess the greatest sum of available tension, are chiefly concerned in the production of *vis viva*, the chief representative of which is animal heat.

If a strong man, previously well fed, entirely abstains from food for twenty-four hours, he consumes muscle corresponding to the expenditure of 8·024 grammes of nitrogen, 3·65 grammes carbon in the liquid excretions, 180·5 grammes carbon in respiration, 50·7 grammes albumen, and 198·1 grammes of fat. With a diet entirely free from nitrogen, consisting of 150 grammes of fat, 300 grammes starch, and 100 grammes sugar (together = 254·68 grammes carbon), there were eliminated in the liquid excreta 8·16 grammes nitrogen and 3·61 grammes carbon; in the solid excretions 18·79 grammes and in respiration 200·50 grammes carbon, so that the body had lost 51·8 grammes albumen, but gained 81·5 grammes fat. On a purely animal diet, nitrogen is retained in the body, and the amount of fat is reduced. A perfect equilibrium between the intake and the outlay in the body of a vigorous man (during muscular rest) is obtained by—

* This process is applicable only if the meat is to be immediately consumed.—[EDITOR.]

Albumen (with 15·5 grammes N.)	100 grammes
Fat	100 „
Starch and sugar	240 „
Water, drunk, and contained in the solids	2535 „
Salts	25 „
	3000

These quantities correspond to 250 grammes meat, 400 grammes bread, 70 grammes sugar, 100 grammes fat, 10 grammes salt, and 2100 grammes water. A man on a mixed diet uses, therefore, 49 grammes albumen and 43 grammes fat more than a similarly hungry man not doing work which promotes digestion. With severe muscular work a man needs very little more albumen, but considerably larger quantities of fat and carbohydrates, than when at rest. This extra consumption of albumen and fat for the work of digestion must be considered in deciding on the value of nutriment. The greater tension-power a certain weight of nourishment introduces which becomes free and available in the organism the higher is its food value.

If we estimate, in animal foods, 100 grammes albumen at 65 pfennige,* 100 grammes fat at 20 pfennige, and in vegetable foods 100 grammes albumen at 15, fat at 4·5, and non-nitrogenous extract at 2·5 pfennige, we have the following values:—

Vegetable Foods.	Chemical Composition in per cent.						1 Kilo. has	
	Water.	Albuminoids.	Fat.	Non-nitrogenous Extractive.	Woody Fibre.	Ash.	Nutritive Value calculated, Pfennige.	Market Price, Pfennige.
Rye meal, fine	13·38	9·06	1·42	74·53	0·63	0·98	33·2	36
„ coarse	15·02	9·18	1·63	69·86	0·62	1·69	37·9	24
Rice	14·41	6·94	0·51	77·61	0·08	0·45	30·0	80
Black bread	43·26	6·12	0·93	46·63	0·17	1·89	21·3	20
Fine wheat bread	26·39	8·62	0·60	62·98	0·41	1·00	28·9	48
Peas	14·50	23·00	2·00	53·50	4·50	2·50	48·7	30
Carrots	91·22	0·79	0·26	6·09	0·86	0·79	2·8	33
Cauliflower	92·34	2·89	0·16	3·02	0·80	0·79	5·2	320
Potatoes	75·77	1·79	0·16	20·56	0·75	0·97	7·5	6

Animal Foods.	Chemical Composition in per cents.					1 Kilo. has	
	Water.	Albuminoids (Proteine).	Fat.	Non-nitrogenous Extractive Matter.	Salts	Nutritive Value calculated, Pfennige.	Market Price, Pfennige.
Beef, loin	73·48	19·17	5·86	0·11	1·38	136·3	160
„ 2nd quality	65·11	17·94	15·55	0·62	0·78	143·9	144
„ 3rd quality	71·66	18·14	7·18	—	3·02	132·3	86
„ heart	71·41	14·65	12·64	0·32	0·98	120·5	100
„ liver	71·17	17·94	8·38	0·47	2·04	133·4	50
Ham (pig)	48·71	15·98	34·62	—	0·69	172·1	300
Hare, loin	73·82	23·54	1·19	0·47	1·07	143·4	221
Fieldfares	73·13	22·19	1·77	1·39	1·52	147·8	600
Herring	47·12	18·97	16·67	—	17·24	156·6	105
Sardines	51·77	22·30	2·21	—	23·72	149·3	465
Frankfurt sausage	42·79	11·69	39·61	2·25	3·66	155·2	360
Blood sausage	49·93	11·81	11·48	25·09	1·69	76·4	60
Eggs	72·46	11·36	13·40	1·73	1·05	106·6	200–240
Milk	88·00	3·20	4·00	4·00	1·80	33·6	15
Butter	12·00	0·50	86·00	0·50	1·00	176·9	200–240
Cheese	36·00	23·00	37·00	—	4·00	223·5	150–200

* 100 pfennige = 1*s*.

According to this table the fattest kinds of meat are most to be recommended; game and poultry are very costly; fish cheap in proportion to nutritive value. Sausage and smoked meats are dearer than fresh meat. Milk and cheese are cheap.

Legumens are cheap in proportion to nutritive value. Wheat and rye are cheaper than rice; vegetables (cauliflower, carrots, &c.) the most costly. Meat, eggs, and milk are most completely utilised; vegetables much less thoroughly, as from 20 to 40 per cent. are excreted undigested. A powerful body can scarcely be built up and maintained on a purely vegetable diet. The small capacity for work of persons so fed is known.

SECTION VII.

CHEMICAL TECHNOLOGY OF FIBRES.

WOOL.

Origin and Properties of Wool.—Wool is distinguished from hair chiefly by the three following properties: it is finer; it is not straight, but curled; while it generally contains less pigment, and hence is white in colour. The quality of wool improves with the increase of these three characteristics. Wool, like hair, exhibits an organised structure, consisting histologically of an epithelium, of a rind, and of a pith or marrow. The epithelium of wool consists of small thin plates which overlap each other like the tiles on a roof; in this manner the cuticular plates give to the surface a squamose appearance, which may be coarsely represented as the appearance exhibited by a fir-cone. Fig. 542 exhibits a piece of wool of an ordinary sheep; while Fig. 541, magnified to the same number of diameters, exhibits a

Fig. 541.



Fig. 542.



Fig. 543.



piece of the very finest Saxony wool, thus showing the great difference of fineness of these two sorts of wool. The grooves on the surface of the wool are the cause of its rawness to the touch, and from the existence of these grooves wool admits of being felted. When the fibres which exhibit this texture are pressed together with a kind of kneading motion, and at the same time softened by the action of steam, they join to each other in the direction of the scales on

their surface and, becoming entangled, form a firm, dense texture, which is termed felt.

Coarser wools have also longitudinal grooves, as shown in Fig. 543.

The varieties of wool obtained from animals other than sheep are :—

(*a*) Cashmere wool; the fine downy hair of the Cashmere goats inhabiting the eastern slopes of the Himalaya, from 14,000 to 18,000 feet above sea level. The colour is white-grey or brown. In the state in which it is sent to Europe it is largely mixed with coarse hair, so that, after sorting and cleansing, 100 kilos. of the raw material yield only 20 kilos. of fine hair.

(*b*) Vicuna wool; the very slightly curly hair of the llama or vicuna goat (*Auchenia vicuna*), a native of the high mountains of Peru, Chili, and Mexico. This kind of wool, or rather woolly hair, was formerly more used than now for weaving fine tissues. Sometimes a mixture of ordinary wool and the finest hair of hares and rabbits is substituted for this wool. What is now termed viguna or vicuna wool in the trade is a tissue made of a mixture of wool and cotton.

Fig. 544.



Fig. 545.



(*c*) Alpaca wool, or pacos hair; the long, sleek, white, black, or brown hair of the alpagua or alpaco (pako), a kind of goat which dwells in Peru. This kind of woolly hair has great similarity with the vicuna wool, but is not quite so fine.*

(*d*) Mohair, or so-called camel's wool; the long, slightly curly, silky hair of the angora goat (*Capra angorensis*), a native of Asia Minor. This substance is spun and woven into non-fulled tissues (camlet or plush), and is also mixed up with the half-silk tissues of which it forms the woof or weft.

Chemical Composition of Wool.—Purified and cleansed wool consists chiefly of an albumenoid sulphur-containing substance termed keratin (horny matter), but, as met with on the animals, wool contains much dirt, dust, and suint. The labours of Faist, Reich, Ulbricht, Hartmann, Märcker, and E. Schulze have greatly increased our knowledge of this substance.

The following results are those obtained by Faist when analysing various kinds of merino wool :—

* The microscopical texture and properties of this kind of hair have been investigated and are described in Wiesner's work, *Einleitung in die technische Mikroskopie.* Vienna, 1867, pp. 172 *et seq.*

	1.		2.			
	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Mineral matter . .	6·3	16·8	0·94	1·3	1·0	1·2
Suint and fatty matter .	44·3	44·7	21·00	40·0	27·0	16·6
Pure wool . . .	38·0	28·5	72·00	56·0	64·8	77·7
Moisture	11·4	7·0	6·06	2·7	7·2	3·5
	100·0	100·0	100·00	100·0	100·0	100·0
Percentage of pure air-dry wool .	49·4	35·5	78·06	58·7	72·0	82·2

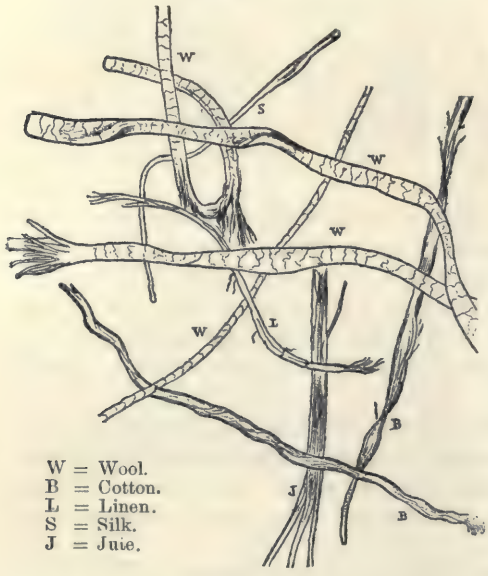
1. Raw wool, air-dried.—(*a*) Hohenheim wool, with a small quantity of readily soluble suint. (*b*) Hohenheim wool (the name of a large agricultural establishment and agronomical school near Stuttgart, Würtemburg), containing a large quantity of glutinous suint. 2. Washed wool, air-dry.*—(*c*) Hohenheim wool. (*d*) Same variety, with difficultly soluble suint. (*e*) Hungarian wool, very soft. (*f*) Würtemburg wool, less soft.

While making researches on wool, Elsner of Gronow estimated the loss which wool experiences when treated with sulphide of carbon for the elimination of the suint. The results were—

Washed merino wool *	15 to 70 per cent.
Unwashed wool (*laine en suint*, raw wool) .	50 to 80 „
Long carded wool	18 „

Suint is a mixture of secreted and accidental substances, dust, &c. When raw wool is macerated for some time in warm water, there results a turbid liquid which contains suspended as well as dissolved matters. The dry substance of the aqueous extract of suint consists, according to Märcker and Schulze (1869), of—

Fig. 546.



W = Wool.
B = Cotton.
L = Linen.
S = Silk.
J = Jute.

	1.	2.	3.	4.
Organic matter .	58·92	61·86	59·12	60·47
Mineral matter .	41·08	38·14	40·88	39·53

1 and 2 relate to wool of mountain sheep.
3 and 4 to full-bred Rambouillet sheep.

The soluble portion contains the potash salt of a fatty acid (*potassium suintate*). The fatty acids contained in suint are, according to Reich and Ulbricht, mixtures of oleic and stearic acids, probably also palmitic acid and a small quantity of valerianic acid, with potash in such quantity, that more recently this material has been employed for obtaining therefrom potassium carbonate and potassium chloride. 100 kilos. of raw wool may yield from 7 to 9 kilos. of potash (see p. 283).

Artificial Wool is formed by tearing up woollen rags, and is used in very considerable quantities both along with, and instead of, fresh wool. The trade dis-

* Washed on the sheep while alive, an operation performed by the farmers, and to be distinguished from the washing wool undergoes during manufacture.

tinguishes *shoddy*, the artificial wools obtained by tearing up into a fibrous state all sorts of fabrics known as "softs"—*i.e.*, blankets, flannels, old stockings, &c. *Mungo* is obtained by grinding up the "hard" rags from milled cloths. Fig. 546 shows the mixed fibres obtained by tearing up cloth.*

SILK.

Silk is at once distinguished from cotton, flax, hemp, and wool by being naturally produced as a very long and continuous thread, whereby the operation of spinning is dispensed with; but in its stead the operation known as silk-throwing is required, by which several of the natural fibres of the silk are twisted into one in order to obtain a stouter yarn.

Silk is the produce of the silkworm (*Bombyx mori*), an insect which undergoes four metamorphoses. The worm is produced, in the spring, from the egg, or ovule. It casts its skin from three to four times, and finally spins a thread, produced, or rather secreted, by two glands placed near the head, from small apertures, in which is glutinous fluid, which immediately coagulates under contact with air. Thus, what is termed a cocoon is formed, which serves as a shelter for the pupa against injury and cold. The thread is double, but is united in one by a peculiar kind of glue termed sericin, which is laid as a kind of varnish over the whole surface of the thread, of the weight of which it forms about 35 per cent. After a period of from fifteen to twenty-one days, the pupa is metamorphosed into a butterfly, which, in order to leave its prison, softens a portion of the cocoon with a juice which it secretes, and then perforates the softened part. For the purpose, however, of producing silk, the pupa is not allowed to develop so far, but is killed (excepting in a number of cocoons intended for the full development of the moths, so that they may produce eggs), and the thread of the cocoon is carefully wound on a reel.

Sericiculture.—*Varieties of Silkworms.*—The *Bombyx mori* is the main supplier of silk. Its food is the leaves of the white mulberry tree, *Morus alba*. There are, however, other silk-producing insects, among which the following are to be noticed:—

(*a*) *Bombyx cynthia*, largely cultivated by the natives of the north-east portion of the interior of Bengal and also by the Japanese. The former call this worm *Arrindy-arria*, the latter *Yama-maï*. This worm feeds on rice leaves, and on *Ricinus communis*. The silk obtained from this insect, although less brilliant than that which the ordinary silkworm yields, is very useful, as being durable and strong. This worm will feed on other leaves, such as that of the weavers' thistle, *Dipsacus fullonum*, wild chicory, *Chicorium intibus*, and the leaves of the *Ailanthus glandulosa*. The results of acclimatising this insect in France and Germany have been satisfactory.

(*b*) *Bombyx pernyi* is a native of Mongolia and China; it feeds on oak-leaves. Some years ago these worms were introduced into France, and have been fed and reared successfully upon European oak-leaves.

(*c*) *Bombyx mylitta*, or Tussa worm, is a native of the colder parts of Hindostan and of the slopes of the Himalaya. Its silk is an important article of commerce in Bengal. This insect feeds on oak and other leaves, casts its skin five times, and yields large cocoons. The fibre of this kind of silk is from six to seven times stouter than the silk of the ordinary worm, but unfortunately the Tussa worm only lives in its free natural state, and when captive does not produce silk. The following silk-producing varieties belong to North America:—(*d*) *Bombyx polyphemus*; on oak and

* For full information on wool from an industrial point of view, the reader may compare *The Structure of the Wool Fibre in its Relation to the Use of Wool for Technical Purposes*, by Dr. F. H. Bowman, F.L.S., &c. Manchester: Palmer and Howe.—[EDITOR.]

poplar trees. (*e*) *B. cecropia;* on elm, whitethorn, and wild mulberry trees. (*f*) *B. platensis;* on a kind of mimosa, *Mimosa platensis.* (*g*) *B. leuca*, which deserves further attention.

We quote the following account of the culture and rearing of silkworms:—(1) The mulberry tree. The leaves of the variety known as the white mulberry tree, from the fact that its fruit is yellow or light red in colour, is the most suitable food for this insect, but its cultivation belongs to horticultural pursuits, and we cannot enter upon the subject here. (2) The production of the eggs or ova of the silkworm is effected in the following manner:—The largest and finest cocoons, and such as have a fine thread, are selected and preserved; usually the cocoon of the female insect is more oval than that of the male, which is more pointed at the ends and is somewhat depressed in the centre. Although these characteristics do not apply in all cases, sericiculturists become sufficiently adepts in this matter to be able to select a sufficient number of cocoons of each sex. 100 to 120 pairs of well-formed cocoons yield 30 grammes of eggs, about 50,000 in number, from which, however, only 70 to 75 per cent. of worms are obtained. The cocoons selected for breeding purposes are allowed to remain on a table covered with a white cotton cloth. After some twelve days the moths make their appearance, and, having paired, the females, after a lapse of some forty hours, lay from 300 to 400 eggs. (3) The eggs are properly protected from cold in winter and remain in the buildings called *magnaneries*, being placed in a uniform layer on a cotton cloth stretched on a wooden frame. The eggs are covered with sheets of white paper, perforated with small holes. Upon the sheets of paper mulberry leaves, at first cut up so as to form a kind of chaff, are placed. In France a contrivance known as a *couveuse*—that is to say, an oven, in which a suitable temperature is kept up—is now generally used for the purpose of breeding the worms, which are best hatched from the eggs at a temperature of 30°, provided moisture is also present. The young brood, on leaving the eggs, creep through the holes in the paper, and seeking daylight (there is always free access of light in magnaneries) begin at once to feed on the mulberry leaves. (4) The rearing of the worms requires care and attention. They are best placed on paper laid on wooden frames. The worms grow rapidly, and are very voracious. They cast their skins four times, and after from thirty to thirty-two days begin to spin the cocoons. (5) When the period of spinning approaches, the worms are placed in small, somewhat conical wicker-work baskets, in which they are comfortably located. The first thread spun, or rather an entangled flocky mass, is afterwards separately collected and kept as floss silk. The insect discharges, before beginning to spin further, first a solid substance, white or green in colour, and consisting, according to Péligot, chiefly of uric acid; next a clear, watery, very alkaline liquid, which contains 1·5 per cent. of potassium carbonate, this curious discharge amounting to from 15 to 20 per cent. of the weight of the worm. The formation of the cocoon is finished in about five days, but the cocoons are not collected for the purpose of reeling the silk until after seven or eight days, so as to make sure that all the worms have spun.

As far as the chemical composition of silk is concerned, we have to distinguish between the fibre and its envelope. The fibre consists, for about half its weight, of fibroin, a substance which, according to Städeler's researches, is nearly related to horny matter and mucus, and is identical with these as regards chemical composition. The formula of silk fibroin is $C_{15}H_{23}N_5O_6$. The gum-like envelope of the silk fibre, which has been termed by Cramer and Städeler silk glue or sericin, is partly soluble in water and readily so in soap-suds and other alkaline fluids. The formula of sericin is $C_{15}H_{25}N_5O_8$. P. Bolley's researches have proved that in the silk-producing and secreting glands of the worm only glutinous, semi-liquid fibroin occurs, which, on coming into contact with air, is acted upon by the oxygen, and

then converted into sericin. Raw silk leaves, on ignition, a small quantity of ash; Guinon found in Piedmontese raw silk, dried at 100°, 0·64 per cent. of ash, consisting of 0·526 lime and 0·118 alumina and oxide of iron. Dr. J. G. Mulder found in 100 parts of raw silk—

	Yellow Silk from Naples.	White Silk from the Levant (Almasin Silk).
Fibroin	53·40	54·0
Glue-yielding matter	20·70	19·1
Wax, resin, and fatty matter	1·50	1·4
Colouring matter	0·05	—
Albumen	24·40	25·5

(6) *Killing the Pupa in the Cocoon.*—The pupa remains in the cocoon for from fifteen to twenty days, and is then metamorphosed into a butterfly, which will perforate the cocoon, and thus obtain an exit. It is clear, however, that the cocoon not intended for breeding purposes should not be kept so long, because by the perforation of the cocoon the silk is spoiled, or at least greatly deteriorated. Therefore the pupæ in the cocoons are either killed by the application of oven-heat or of steam.

Manipulation of the Silk.—Six different operations are required to render raw silk fit for use as an article of commerce and suitable for weaving, &c. These operations are :—

(1) *The Sorting of the Cocoons*, an operation which requires great care and greater experience, its aim being—(*a*) the separation of yellow from white cocoons; (*β*) the elimination of all damaged cocoons as only fit for yielding floret silk; the damage may arise in various ways, as, for instance, by mouldiness, injury by other insects, and, lastly, fouling of the pupa, as well as perforation by the moth; (*γ*) selection of the cocoons according to varying fineness of thread and uniformity of the silk.

(2) *Winding the Silk on the Reel* is the first operation with the cocoon. By this the threads of silk which the insect has wound up into a kind of ball are unwound and brought into the shape of a skein or strand.

As the single fibre of silk is far too thin to be manipulated, the operator usually takes from 3 to 10 or even 20, making them unite by the operation of reeling. This is not by any means so readily performed as might be imagined, because it is difficult to find the end of the thread, whilst the surface of the cocoon is varnished with a gum-like mass, which glues the fibres together. Partly by the aid of hot water and partly by dexterity these difficulties are overcome, and by good management a thread of from 250 to 900 metres length may be obtained from each cocoon, each yielding from 0·16 to 0·20, at the very utmost 0·25 gramme, of raw silk. 1 kilo. of raw silk requires from 10 to 12 kilos. of cocoons. The silk thus obtained is termed raw silk, which should be quite uniform as regards thickness and strength of fibre. That portion—the interior and a portion of the outer layer of the cocoon—which does not admit of being reeled off is employed for making floret silk, by operations similar to those in use for wool and cotton—viz., cleansing, disentangling, combing, carding, and spinning, to produce a silk yarn.

(3) *The Throwing of Silk.*—As the thread obtained by reeling is too fine for use, either for weaving, knitting, sewing, &c., it is usual to unite several threads of silk by means very similar to those used in rope-making, an operation termed throwing, known as twisting when the thread of raw silk is simply rotated on its axis so as to make it stronger. The following are the chief varieties of thrown silk :—(*a*) Organzine, used as chain for woven silk fabrics, is prepared from the best raw silk. The threads of from 3 to 8 cocoons are united, being first strongly twisted and next thrown, after which two of such threads are twisted together. (*b*) Trame used for woof or weft, and for silk cord, is made from inferior cocoons. Single-threaded trame consists of one single twisted raw silk thread made up of the united threads of from 3 to 12 cocoons. The double-threaded trame consists of two threads twisted to the left, but less strongly than in

organzine. There are also three-threaded trame, &c. Trame is softer and smoother than organzine, and therefore fills better than round threads in weaving. (*c*) Marabou silk is stiffly thrown and similar to whipcord; it is made from three threads of the whitest raw silk and thrown in the trame fashion; is dyed without being previously scoured (boiling the gum out in this instance), and is again thrown after dyeing. (*d*) Poil silk is a simple raw silk thread, twisted, and chiefly used as a basis for gold and silver wire, such as is worn on military uniforms. Sewing silk is obtained from some 3 to 22 cocoon threads being twisted together. There are several other varieties of silk thread used for crochet, knitting, &c.

(4) *Conditioning or Testing of Silk.*—The fineness of raw as well as of thrown silk is expressed by stating how many yards or metres length of the fibre are contained in a certain weight. The unit abroad is 400 ells or 475 metres. When the expression is used, that such silk is at 10 grains, it is understood that 475 metres length of that particular silk weighs 10 grains; a silk at 20 grains has the same length but double the weight, and consequently that silk is only half as fine as the former.

Raw, as well as thrown silk, contains a large quantity of hygroscopic water, the quantity of which cannot be judged by the external appearance of the material. The silk usually met with in commerce contains from 10 to 18 per cent. of hygroscopic water; and silk may occasionally contain even 30 per cent. without appearing to be moist. As silk is a very expensive material and often sold by weight, it is clear that this property of taking up water is too important to be left unnoticed; and for that reason silk is conditioned as it is called, that is, the quantity of water it contains is duly ascertained.

(5) *Scouring or Boiling the Gum out of Silk.*—Excepting a few instances, such as for example, in the weaving of fine silken sieve cloths, and for crape and gauze fabrics, raw silk has to be deprived of its envelope, the gummy matter already mentioned, in order to give softness, suppleness, gloss, and especially also to render the silk fit for being dyed.

The operation of scouring is comprised in the following manipulations:—

(1) Removing the gum.
(2) Boiling.
(3) Colouring.

The taking out of the gum is performed in the following manner:—Olive oil soap is first dissolved in hot water and into this solution at 85° the skeins of silk are placed hung on sticks. The skeins are moved about in this bath until all the gum has been uniformly taken out. The silk is next wrung out, rinsed in fresh water and then dried. Silk may by this process lose from 12 to 25 per cent. in weight, according to the quality of the raw silk and the quantity of soap employed. The scoured silk is ready for dyeing with dark colours, but if required to be dyed with bright colours it has to be first boiled. To this end it is put into coarse canvas bags, each containing from 12 to 16 kilos. of silk, and in these sacks the silk is placed in a soap bath and boiled for 1½ hours: the silk is next rinsed in water, wrung out, and dried. The operation of rosing or colouring aims at imparting to the silk a slight tint in order to enhance its beauty. The trade distinguishes various hues of white silk, such as Chinese white, azure white, pearl white, &c. The first of these hues, a somewhat ruddy tint, is obtained by rinsing the silk in soap-water, to which some annatto has been added. The bluish hues are produced by indigo solutions. The bleaching of scoured silk is effected by the aid of sulphurous acid, the fibre either being placed in a room where this gas is evolved from burning sulphur, or by treating the silk with an aqueous solution of the acid. As silk loses a great deal in weight as well as in body by the scouring, which is, however, required, because raw silk does not permit of being dyed, it has become the practice to produce a material called *souple*, obtained by treating the raw silk with boiling water

in which only a small quantity of soap, 1 kilo. to 25 kilos. of silk, is dissolved. Instead of this soap solution, an acidified (with dilute sulphuric acid) solution of magnesium or sodium sulphate is sometimes used. The silk loses by this process only from 4 to 10 per cent. in weight. In order to bleach raw silk without depriving it of its natural rigidity, the skeins are digested at a temperature of from 20° to 30° with a mixture of alcohol and hydrochloric acid; this liquor becomes green in colour, and the deeper the hue the whiter the silk. The silk is rinsed in water, and having been dried will be found to have lost only about 2·91 per cent. in weight. The alcohol used in this process may be readily recovered by neutralising the acid with chalk and subsequent distillation.

Means of Distinguishing Silk from Wool and from Vegetable Fibres.—Owing to the manufacture of mixed fabrics, it has become a necessity to be enabled to detect and distinguish silk from woollen as well as from cotton and linen fibres. Microscopical investigation aided by chemical tests is resorted to for this purpose.

The animal fibres (silk, wool, and alpaca) are at once distinguished from the vegetable (flax, hemp, cotton), by the fact that the former are soluble in caustic potash and the latter not. The animal fibres on being singed give off a smell of burnt feathers, and when ignited in the flame of a candle are almost immediately extinguished, a carbonaceous residue being left. Cotton and linen fibres continue to burn, do not give off the smell of burnt feathers, and do not leave a carbonaceous mass when extinguished. Wool and silk are coloured yellow by nitric acid (1·2 to 1·3 sp. gr.), cotton and linen not so. Nitrate of protoxide of mercury colours animal fibres intensely red, and upon the addition of a soluble alkaline sulphuret this colouration becomes black. Linen, or flax, and cotton are not at all acted upon by this reagent. An aqueous solution of picric acid dyes wool and silk intensely yellow, but not so vegetable fibres. The colourless liquid obtained (according to Liebermann) by boiling a solution of magenta with caustic potash does not impart to a mixed fabric of wool and cotton any colour at all; but when the fabric is thoroughly washed in water, the woollen fibre becomes intensely red-coloured, while the cotton fibre remains colourless. A solution of ammoniacal oxide of copper in excess of ammonia dissolves, first silk, next cotton, but not wool. When wool and floret silk are mixed the latter may be dissolved by successive treatment with nitric acid and ammonia, while wool is left. A solution of oxide of lead in caustic potash or soda may serve to distinguish wool from silk, owing to the fact that, in consequence of the former containing sulphur and the latter not, the mixture, when wool is present, becomes black. Sodium nitroprusside is undoubtedly the most delicate test for distinguishing between silk and wool in solution in caustic alkali, because, owing to the sulphur of the wool, this reagent produces in the solution a violet colouration.

By the aid of the microscope, cotton, wool, and silk are readily distinguished from each other. As for cotton, it is fully described on pp. 802, 813, 815, and its microscopical appearance illustrated by woodcuts, as also are silk and woollen fibres. Of the latter we may now state that, whereas cotton fibre consists of only one cell, wool (as also hair and alpaca) is made up of numerous juxtaposed cells; the silk fibre being similar to the secreted matter of spiders and various kinds of caterpillars. The silk fibre (Fig. 547) is smooth, cylindrical, devoid of structure, not hollow inside, and equally broad. The surface is glossy and irregularities are but seldom seen on it. If it is desired to detect in a woven fabric the genuineness of the silk, it is best to cut a sample to pieces, place it under water under the object-glass of a microscope magnifying from 120 to 200 times, covering it with a thin piece of glass. The round, glazed, equally proportioned silk fibre, Fig. 547, is easily distinguished from the unequal and scaled wool fibre (*W* in Fig. 548), and from the flat band-like and spiral cotton fibre (*B* Fig. 549). Under the microscope also the admixture of inferior with superior fibres

of silk can be easily detected. A small microscope known as a "linen prover" is sold for these examinations.*

Fig. 547.



Silk.

Fig. 548.



Wool.

Fig. 549.

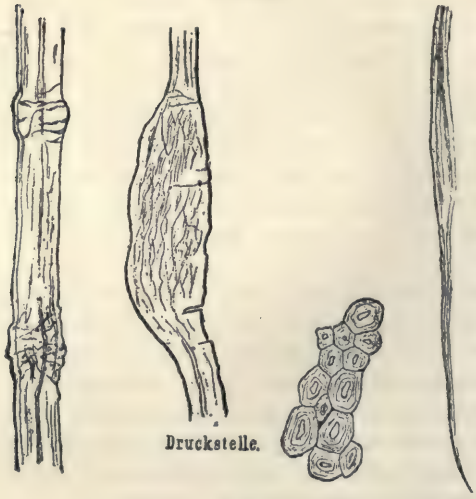


Cotton.

VEGETABLE FIBRES.

Vegetable fibre, essentially cellulose, $C_6H_{10}O_5$, forms the texture of plants. With incrustations it forms woody fibre; in long threads or tufts it appears as flax, hemp, cotton, &c., which constitutes the important groups of vegetable fibres, and serves for the production of tissues, paper, and gun-cotton.

Fig. 550.



Flax.
Druckstelle = Place of pressure.

Flax.—The flax used in spinning is the fibre of the flax-plant, *Linum usitatissimum*, a plant of the class Pentandriæ, order Pentagyniæ, in the system of Linnæus, and the type of the order Linnaceæ in the natural system of Botany. The flax is gathered, tied in bunches, and dried in the fields. After drying the plant is combed with an iron or flax comb, to separate the seeds, and is then bound in thick bunches. The flax fibre used in linen fabrication lies under the bark of the plant, and is surrounded by a gummy substance, or pectose according to J. Kolb, which must be removed by chemical or mechanical means to fit the fibre for industrial purposes. This is done by "softening" or "rottening," by which, according to Kolb, pectin-fermentation is set up, and

* For further particulars on silk Dr. Bowman's work may be consulted; and for an account of the so called wild silks see *Handbook of the Collection of the Wild Silks of India*, by Thomas Wardle (Her Majesty's Stationery Office.)—[EDITOR.]

the pectin converted into pectic acid. The flax is kept under water until the impurities float on the surface, leaving the fibre intact; this is the soaking method. Another method, dew-softening, as it is termed, consists in spreading out the flax in layers to the influence of the atmosphere, water being occasionally thrown over the flax. Both these methods are unsound, as the flax is liable to become rotten, while the impurities are not thoroughly removed.

Hot-water Cleansing.—After many experiments with different chemical substances, an alkaline bath and dilute sulphuric acid have been found the best agents to effect the separation. The flax is placed in large vessels of water heated by steam from 25° to 30°; after standing from sixty to ninety hours the operation is complete. This mode of treatment, aided by an alkaline or acid solution, yields the best results, the value of the process being—(1) That the construction of the fibre is equally affected, rendering the article better suited for manufacture. (2) That the fibre does not lose weight as in the other methods, where 10 per cent. is sometimes lost. (3) That there is a considerable saving in expense.

The *retted* flax, as it is technically termed, consists of cellulose and pectic acid. The next process is termed *scutching*, and includes the separating of the fibre from the woody structure of the stem. The machine for this purpose consists of two parts; the upper of wood, in the form of two splints, working on hinges. Wooden knives are placed under the splints, and are arranged to act upon the fibre by pressure upon a handle.

Beating or Batting the Flax.—Scutching consists of two operations—bruising the flax and beating away the woody parts from the fibre. For the latter operation the Belgian batting-hammer is generally used. It is a deeply grooved wooden block, furnished with a long curved handle. The sheaf of flax is laid on the ground, untied, and spread out, and is beaten with the hammer by the workman. If the flax is not sufficiently loosened by batting, it is submitted to the swinging-block, having a cut at three-fourths of its height serving to hold about a handful of flax. This flax is then beaten with the scutch-blade, a piece of hard, tough wood, generally walnut-wood. Instead of the swinging-block a grinding-knife is sometimes used on an iron block. The knife is formed of a thin blade, and a heavy wooden handle. A bunch of flax is held in the left hand, at an angle for the easy use of knife with which the flax is beaten. Notwithstanding these clarifying processes the bark still adheres to the flax, which has to undergo a further operation, that of combing.

Combing the Flax.—The combing or hackling of the flax removes all the material detrimental to the ultimate spinning of the fibres, and also equalises their length, rendering them smooth and parallel. The combs are made of zinc or steel, and are of varying degrees of fineness, the process commencing with a coarse comb and finishing with a fine one.

Tow, or Tangled Fibre.—However carefully the operation of scutching may be performed, there is always a certain amount of waste resulting from the entanglement of the fibre, and this waste is termed scutching-tow or codilla. It is used in the manufacture of ropes, and for similar inferior purposes. The flax fibre, before it is fitted for spinning, has to be boiled in an alkaline lye, to remove the dirt and grease.

100 kilos. of cleansed flax weigh after

Bruising	45 to 48 kilos.
Scutching	15 „ 25 „
Combing	10 „

Flax Spinning.—The spinning of the combed flax into yarn is effected by hand and by machinery. The combed flax is first placed in bands of equal thickness, and then stretched. The hand spinning-wheel is universally known. The mechanical spinning consists in—(1) Placing the fibres in a parallel series of equal thickness and length

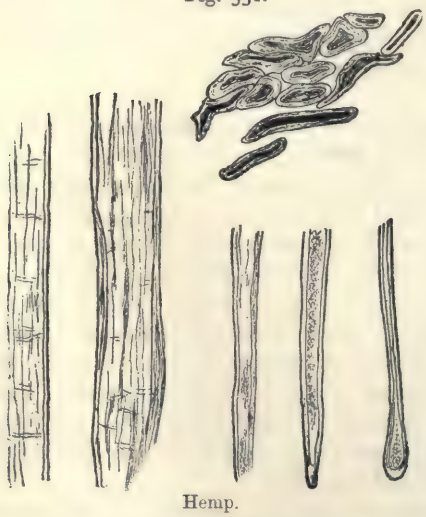
throughout. (2) These bands are stretched, the finer the fabric to be woven the greater being the stretching required. (3) By further stretching and twisting cord is spun. (4) The fine cord is still further stretched and twisted. Tow, or codilla, is spun similarly to the flax, being previously combed and placed in bands of equal length. Flax yarn is either used unbleached or is bleached before spinning. Linen thread is obtained by twisting several cords together.

Weaving the Linen Threads.—By weaving the cords parallel to each other, chain cords are spun. Webbing, wrappers, and thick fabrics are made in this way.

Linen.—Linen is produced by weaving the twisted cord. The selvage is made by the return of the shuttle on each side of the fabric. For coloured fabrics coloured threads are used instead of white, only more shuttles are required, one shuttle to each colour. Linen damask, as well as drill, is woven in various patterns, the difference being that the woof forms the pattern on drill, while chain-cord is used for that of damask. Batiste is a fine linen cloth, slightly thinner than cambric.

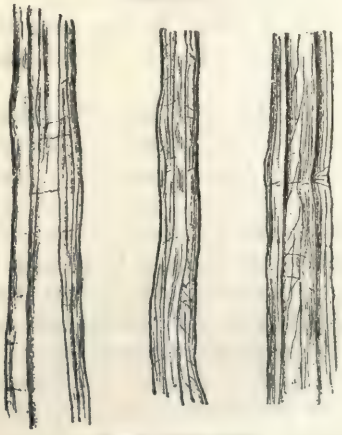
Hemp.—Hemp (*Cannabis sativa*) is chiefly cultivated for the fibre of its inner bark. This fibre, although rough, is very hard and firm, and better adapted for the manufacture of sail-cloth, canvas, rigging, &c., than any other. Its uses for inferior domestic purposes are manifold. The working of the hemp stalk accords essentially with that of flax, being steeped in water, dried and crushed in a hemp mill. By the old method the husk is crushed under a large stone cone moving in a circular course around a vertical axis. The construction of the new hemp mill is more advantageous. The hemp is purified by winnowing and afterwards combing. It is difficult to spin on account of its length, and is woven in two or three parts. Of late various foreign fibres have been used as substitutes, principally the following:—

Fig. 551.



Hemp.

Fig. 552.



Hemp, when spun.

Fig. 553.



Chinese Grass, Tschuma.

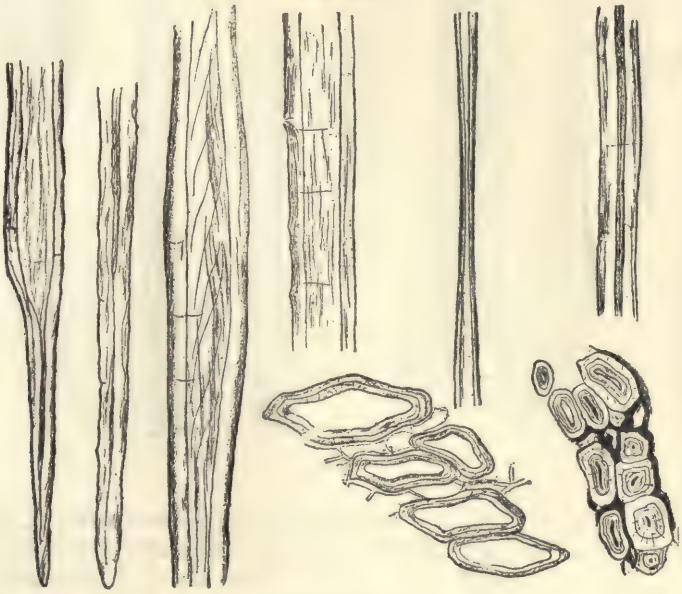
a. Stalk Fibre.

(1) Chinese Grass (*Chinagras, Tschuma*), a fibre from *Urtica s. Boehmeria nivea* and *heterophylla*, which is cultivated in China and the East Indies, Mexico, the Valley of the Mississippi, Cuba, the Wolga Plains in Russia, the South of France, and in Algiers. The Chinese method of treating the fibre is

remarkable. The fibre is not spun, but cut into appropriately small pieces, these being placed end to end, and rolled by the hand until joined together. The fibre is thus rolled quite smooth and does not require pressing. It forms a beautiful texture of singular brightness, called grass linen, or *China grass cloth*. The raw material is of a green or brown colour, but when bleached, can be dyed any colour.

(2) The Great Nettle (Fig. 554), *Urtica s. dioïca*. The interior fibrous pith supplies the material for nettle cloth and muslin.

Fig. 554.



Nettle Fibre.

(3) Ramie Hemp, from *Urtica s. Boehmeria utilis*, is of the nettle species, and a native of Borneo, Java, Sumatra, and other islands of the Indian Archipelago. Of late various experiments as to its mode of manufacture have been tried in Germany. It is from one to two metres in length, of a delicate golden white, and not so bright and stiff as flax.

(4) Rhea Grass, *Urtica s. Rhea tenacissima*, is a native of the East Indies, of little value for manufacture.

(5) Jute (*paut hemp*) is obtained from a lime tree, a native of the East Indies and China, *Corchorus capsularis*, *C. textilis*, *C. olitorius*, *C. siliquosus* (Figs. 555, 556). The fibre for spinning is brown, and in England is used for sackcloth and coarse packing thread. It is not a material adapted for purposes of nautical application, as it has not sufficient firmness to withstand water.

Queensland Hemp, the bast-fibre of various species of *sida*, belonging to the family of the *Malvaceæ*.

(6) Bombay Hemp, from *Hibiscus cannabinus*. The woody fibre of this plant is roasted and separated by means of beating. In England it is used for cordage, rigging, &c.

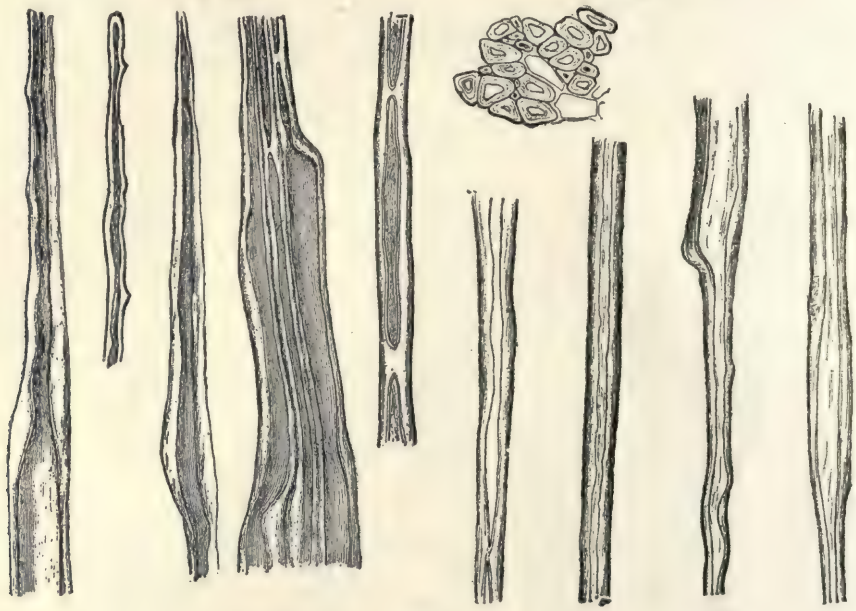
(7) Sun Hemp, Japan, or East Indian Hemp, from *Crotolaria juncea*, resembles other hemp in the length and firmness of its fibre.

β. *Leaf Fibre.*

(8) New Zealand Flaxes (*Phormium tenax*), Fig. 557, are employed in their native country for articles of domestic use. The leaf is straight, the fibre tough, and of a

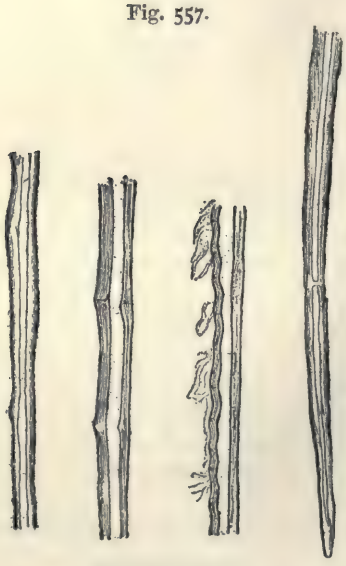
shining white. The prepared material is similar to ordinary hemp in roughness and stiffness.

Fig. 555. Fig. 556.



Jute.

Fig. 557.



Phormium Tenax.

(9) Aloe Hemp (*Agave Americana, A. vivipara, A. foetida, &c.*) is a native of Peru, India, the Antilles, and Mexico, where the leaf, which is generally a yellow-white, is cultivated for its fibre, and used for rope-making.

(10) Manilla Hemp (Feather Fibre) is a native of India and many islands of the Malay Archipelago, and comes from *Musa textilis, M. troglodytarum*, and *M. paradisiaca*. It is commercially known as a yellow-white or brown-yellow fibre, and is from 1·3 to 2·2 metres long. The inside bark is stripped off from the bottom upwards, refined, and combed. The white kind is silky and bright, and is used in the manufacture of damask furniture and various fancy articles.

(11) Ananas Hemp comes from the West Indies, Central and South America, where the common ananas is cultivated, *Ananassa sativa s. Bromelia ananas*, as well as other species. It is rather inferior to some fibres for spinning.

(12) Pikaba Hemp is from the leaf of the *Attalia funifera*, a Brazilian palm. It is used in rope-making.

(13) Cocoa-nut Fibre is a reddish-brown fibrous material, in which the cocoa-nut shell (*Cocos nucifera*) is enveloped. It is very strong and elastic, and is used for matting, ropes, hurdles, &c.

Cotton.—Cotton surrounds the fruit of a shrubby plant of the species *Gossypium*, cultivated in the tropics and the Southern States of America for manufacturing purposes.

The fruit consists of a cup-shaped calyx, enclosed in a three-cleft exterior calyx, bearing a soft white down. Another species, *Gossypium religiosum*, bears a yellow down, used by the Chinese in manufacture. The down is kept separate from the seed when packed for travelling, to prevent its becoming oily and unfit for use. While in a raw state, it is subjected to an operation termed ginning in a saw-gin, to separate the wool from the seed. Whitney's saw-gin consists of from 18 to 20 circular saw-blades, revolving on a horizontal axis about 100 times a minute. The teeth of these saws project through a grating, seize the wool and pull it through, the bars of the grating being too narrow to admit the seed. Twenty saw-blades will clean 400 lbs., and 80 saw-blades, worked by 2-horse power, 500 lbs., raw cotton per day. Of late the carding cylinder is sometimes used instead of the saw-gin. In America oil is largely extracted from the seed, 30 lbs. yielding about 1 lb. of oil. The seed is also used for manure.

Fig. 558.



Cotton, spun. Cotton, unspun.

Species of Cotton.—The quality of cotton is decided by its smoothness, and distinguished by the country from which it is imported. The various kinds are:—North American: Sea Island, or Long Georgia, Orleans, Upland, Louisiana, Alabama, Tennessee, Georgia, Virginia. South American: Fernambuco, Bahia. Columbian and Peruvian. West Indian: Domingo, Bahama, Barthelemy. East Indian: Dhollerah, Surat, Manilla, Madras, Bengal. Levant: Macedonian, Smyrna. Egpytian: Mako or Jümel. Australian: Queensland. European: Spanish and Sicilian.

Substitutes for Cotton.—Substitutes for cotton are found in the black poplar (*Populus nigra*) and the aspen (*P. tremula*); the fibres of the latter are not so elastic as some of the substitutes discovered. The rush (*Juncus effusus*), the German tamarisk, and the thistle (*Agrostis*), the *Salix pentandra*, the *Zostera marina*, and the flax tree, supply material for manufacture. Some twenty years ago Chevalier Claussen endeavoured to open the filaments of flax by chemical action by steeping the fibres in a bath of 1 part sulphuric acid to 200 parts water, and then dipping it into a weak solution of carbonate of soda. By this process the flax is changed into a downy mass resembling cotton in lightness; but the method was not successful, as the firmness of the fibre was injured, and its value deteriorated in other ways.

Detecting Cotton in Linen Fabrics.—There is a great difficulty in detecting cotton in linen fabrics when the fibres are closely interwoven. The old method of testing the presence of cotton in linen was by placing it under a powerful microscope, but chemical analysis presents more reliable methods. The following tests, recommended by Kindt and Lehnert, prove the existence of cotton in linen by absorption. The linen containing cotton fibre is placed in a bath of sulphuric acid of 1·83 sp. gr. for from 1 to 1½ minutes. The cotton fibre is immediately absorbed, the sulphuric acid acting upon it more quickly than upon the linen; the fabric upon being dried has a curled or shrivelled appearance. Other fibres—sheep's wool, silk, and flax—are now treated chemically, and their smoothness and glossiness, which are found to be the greatest preservatives against decay, are attributable to chemical agency. The colour test of Elsner is useful, but not always successful, on account of the transition of the delicate colours being so instantaneous as to make it difficult to form a decision. As a colour

test there may be taken half an ounce of the root *Rubia tinctorum*, *i.e.*, madder, macerated for twenty-four hours in 6 ounces of alcohol at 94 per cent. When filtered, the tincture appears a clear brown-yellow. Pure linen fabrics immersed in it become a dull orange red, and pure cotton yellow; the flax fibre will assume a yellow red, and the cotton a bright yellow, the fabric appearing not uniform in colour but streaky. When the fabric becomes so unequally streaked as to make it difficult to discern whether it be linen or cotton, the following test will prove decisive:—Place the streaky fabric in a solution of spirits of wine, and then in a weak solution of aniline red, by which it becomes coloured, and finally let it remain from one to three minutes in a weak solution of sal ammoniac; the colour of the cotton fibre will be dissipated and the linen will become a beautiful rose red. From Elsner's first test for change of colour the method of previously colouring the linen fabric was established. Cochineal was selected for this purpose, and the linen placed in a weak solution, chloride of lime being used to prevent the colour in the linen running, while the cotton contained in the fabric changes colour immediately. Frankenstein's oil test for uncoloured fabrics can be recommended for its simplicity and excellence. The fabric is dipped in olive or rape-seed oil; it quickly becomes soaked through, and the surplus oil is removed by blotting-paper, the linen fibre becoming transparent, leaving the cotton opaque. When an unbleached fabric is tested in this manner it appears shining at first, but becomes dimmer in the parts where the cotton is present. A truer method of testing, however, is given by the magnifying glass. Böttger gives a test with potash. The linen fabric is immersed in a concentrated solution of potash; in about two minutes it becomes a deep yellow, the cotton fibre assuming a light yellow.

Stöckhardt gives a spirit test. Linen fabrics are placed in layers with lighted brandy; the linen fibre extinguishes the flame, while the cotton acts as a wick, absorbing the spirit. This experiment can be successfully used with coloured materials, with the exception of those coloured with chrome yellow, lead chromate. The singeing test requires the most delicate treatment. The fibre is placed in a glass vessel over the flame of the spirit-lamp until it becomes a light yellow; then by microscopic examination the cotton fibres will be found curled up, while the flax fibres are distended and clearly separated from each other. Hemp and flax act in the same manner, but do not separate so much. Nitric acid can be so applied as to leave the flax fibre unchanged in colour, while the hemp immediately becomes a pale yellow, and the New Zealand flaxes, *Phormium tenax*, a blood red. The admixture of cotton in linen fabrics is detected by the following test, the discovery of O. Zimmermann:—Place the fabric in a mixture of 2 parts saltpetre and 3 parts sulphuric acid for from eight to ten minutes, then wash, dry and treat with alcohol containing ether. The cotton so treated is soluble as collodion, the linen fibre is not.

Separation of Animal and Vegetable Fibres by Means of Singeing.—The mixture is placed near a bright flame to singe until the hair is consumed, leaving a black ashy mass in the same proportion as the fibre, if it be mixed with sheep's wool.

Animals and flaxen fibres are separated by boiling in potash, which loosens the filaments of wool or silk, leaving the cotton and linen fibres unaltered. Pohl gives us the following test:—Place the fibres in a solution of picric acid for one minute; then carefully wash; the wool or silk filaments will have turned yellow, the cotton or flax fibre remaining white; this can be applied to mixed fabrics. The most certain method is examination under the microscope, where the linen fibre appears in a cylindrical form and never flat; it is not stiff or twisted, and is chiefly characterised by the narrowness of its inner tube. Hemp is similar to flax fibre, being easily broken; its ends branch out stiffly, and its tube is open. The fibres in cotton fabrics are long, of a close thin texture, like a twisted band. Sheep's wool under the microscope appears thicker

than the other filaments, having a perfectly circular stalk with tile-shaped scales. The silken fibre, Fig. 559, is a slender column, smooth on the exterior and easily distinguishable from wool, Fig. 561 representing a mixed silken and woollen fabric, as it appears under a low power. Wool and cotton, Fig. 560, are also easily distinguished from one another.*

Fig. 559.



Fig. 560.

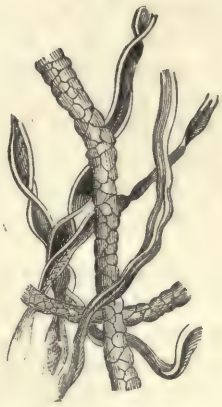


Fig. 561.



Adulteration of Cotton Fabrics.—No other name can be given to the dressing cottons with salts of magnesium, china clay, &c., to an extent sometimes exceeding 50 per cent. This practice is carried to such a length that the finished goods are sometimes sold for a lower price than the same weight of raw cotton.†

BLEACHING.

The operation of bleaching aims at more or less perfectly whitening or decolourising the yarns spun from flax, hemp, jute, cotton, or the textile fabrics woven from the same. Vegetable fibre resists the action of most chemical agents in use in bleaching, while the foreign or incrustating or colouring matters, occurring chiefly on the surface of the fibre, are rendered soluble or completely destroyed. The bleaching of the fabrics and fibres which, such as linen or cotton tissues, consist mainly of cellulose, is based on this principle. The method of bleaching wool and silk differs from that of the vegetable fibres, inasmuch as the chemicals used for the latter would exert upon the former a solvent action, not only as regards the impurities, but the substance itself.

Grass Bleach.—The agent in natural or grass bleaching is apparently ozone, or doubtless more accurately hydrogen peroxide. In this process the formation of ozone is due to the decomposition of water in consequence of the action of light.

Chlorine Bleach.—Schützenberger regards chloride of lime as an oxidising agent, and not as a source of chlorine. Without the co-operation of an acid it is split up into calcium chloride and oxygen ($CaOCl_2 = CaCl_2 + O$), which latter destroys the colouring matter. Witz remarks hereby that the slightest trace of carbonic acid

* For further information the reader is referred to *The Structure of the Cotton Fibre in its Relation to Technical Application*, by Dr. F. H. Bowman, F.L.S., F.C.S., &c. Manchester: Palmer & Howe.

† See *Sizing and Mildew in Cotton Goods*, by G. E. Davis, C. Dreyfus, and P. Holland; Manchester: Palmer & Howe; and *The Sizing of Cotton Goods*, by W. Thompson; Manchester: J. Heywood. It must not be forgotten that the sizing and dressing of cottons in England is not carried to the same extent as the "loading" and "weighting" silks on the Continent—a fraud the more reprehensible as the genuine article is so much more expensive than cotton.—[EDITOR.]

makes the chloride of lime much more efficacious. Without the presence of carbonic acid in the atmosphere, chloride of lime is inactive in certain bleaching processes. Whilst the hypochlorous acid gives off oxygen there is hydrochloric acid formed, which in turn reacts upon the chloride of lime, and so continuously increases its action, which would end in complete combustion of the organic matter. A. Girard ascribes the destructive effects of chloride of lime to the formation of hydrochloric acid, which remains free in spite of the presence of $CaCO_3$ and $CaOCl_2$, hydrating the cellulose and converting it into brittle cellulose. Witz shows that ozone produces the same modifications of cellulose as does chloride of lime; in this case hydratising acids are not present, and consequently Girard's suppositions cannot hold good.

Witz warns us against baths of chloride of lime which are too strong or too prolonged, and which, if applied unequally and under the influence of air and light, have inevitably a destructive action. In practice a strength of 0·7° Tw. should not be exceeded. Hunter shows that chloride of lime is cheaper than permanganic acid and similar oxidising agents.

In order to strengthen the action of solutions of chloride of lime, G. Lunge recommends the addition of acetic or of formic acid. The price of the acid need scarcely be considered, as only a small quantity is required. There first result from acetic acid and chloride of lime free hypochlorous acid and calcium acetate; during the action the former gives up oxygen, and is converted into hydrochloric acid, which, in conjunction with the calcium acetate, is at once transformed into calcium chloride and free acetic acid; the latter acts anew upon chloride of lime:

$$(1)\ 2CaOCl_2 + 2C_2H_4O_2 = Ca(C_2H_3O_2)_2 + CaCl_2 + 2HOCl,$$
$$(2)\ 2HOCl = 2HCl + O_2,$$
$$(3)\ Ca(C_2H_3O_2)_2 + 2HCl = CaCl_2 + 2C_2H_4O_2.$$

The hydrochloric acid produced according to equation (2) is never present in a free state, as it at once reacts upon calcium acetate as in equation (3). This is very important, as hydrochloric acid attacks the fibres on prolonged contact, whilst acetic acid is perfectly harmless. As no insoluble calcium salts are present, the treatment with acids after bleaching is dispensed with; this not merely economises acid and the trouble of the subsequent washing, but it obviates the danger—especially in the case of thick goods—of any traces of acid being left adhering to the fibre. Such traces become concentrated on drying, and attack the fibre, besides being injurious in various dyeing operations. The acid can be applied in various ways—*e.g.*, by adding a small quantity to the solution of chloride of lime at the outset, and at the end of the ordinary treatment with chloride of lime; by passing the goods (prior to washing) through water containing a very small trace of acetic acid; or by placing them in water very slightly acidulated with acetic acid, and gradually running in the solution of chloride of lime with constant agitation. If the goods to be bleached retain a little alkali from the previous bowking, or if the water is very hard, or if the solution of chloride of lime contains appreciable traces of caustic lime, important quantities of acetic acid would be required to neutralise the bases before hypochlorous acid can be set free. In such cases acetic acid can be economised by using a portion of sulphuric or hydrochloric acid in its place, taking care, however, that no free mineral acid is present, but merely acetic acid. This is easily reached in practice by keeping the reaction very faintly acid to litmus-paper.

According to Lunge the removal of the last traces of the bleaching agents from fibrous goods may be effected by means of hydrogen peroxide. On bleaching with chloride of lime the hydrogen peroxide gives off its active oxygen along with that of the hypochlorous acid, whereby the latter (or its salts) is destroyed. Hydrogen peroxide can also be used as "antichlore" in bleaching vegetable fibre or paper stuff in

order to increase the durability of the bleached goods, and to remove the smell of bleach without the disadvantages of other "antichlores."

Sulphurous acid bleaches by masking the colouring-matter, and in few cases only by its destruction. The colouring matters of many blue and red flowers, fruits, &c., form colourless combinations with sulphurous acid; but the colour is merely concealed, not destroyed; dilute acids, nitrous vapours diluted with air, chlorine, bromine and iodine, and the mere action of heat, destroy the bleached sulphurous compounds, and the original colour re-appears. The colouring-matters of yellow flowers are not bleached by sulphurous acid. The same is the case with the green of plants (chlorophyll). Many dyed tissues, such as indigo blue and carmine, are at first not affected by sulphurous acid, but bleaching ultimately takes place, the colouring matters being oxidised under the influence of light. Bleaching with sulphurous acid, as it is industrially carried out, is not a *fast*, but merely a fugitive process, which disguises the colours to the eye. On mere exposure to the air, the sulphurous acid gradually disappears from the bleached goods, especially after previous friction, so that many bleached tissues resume their original colour spontaneously. Lunge recommends the removal of the fixed sulphurous acid by a weak solution of hydrogen peroxide.

For bleaching, the goods are suspended in the sulphuring chamber on rods in a moist state as they come from the centrifugal machine after washing. They are covered with a layer of thick cloth, which is removed from time to time. After filling the sulphur chamber (stove) the necessary quantity of sulphur is placed in an iron pot in one corner, set fire to, and the chamber is tightly closed. The sulphur burns as long as there is sufficient oxygen present in the chamber and the sulphurous acid condenses upon the moist fibre. According to Moyret sulphurous acid acts only at the moment of condensation, and he compares it with the action of an acid in the nascent state, and he describes the alleged inertness of sulphurous acid in solution to the absence of this circumstance. According to Lauber gaseous sulphurous acid owes its stronger action merely to the circumstance that in the gaseous condition it comes in contact with the slightly moistened fibre in a very concentrated state, whilst the solution of sulphurous acid finds its limit at the point of saturation.*

According to the desired purity of the whites the goods are left in the stove for twelve, twenty-four, and even more hours. The cover of cloth serves to prevent any drops of sulphuric acid formed on the roof of the stove from falling upon the goods and destroying them at the point of contact. When the process is completed the air of the stove is forced into the chimney of the works by means of a blast, and the goods are freed from sulphur by taking them through dilute hydrochloric acid at a hand heat. Any yellow spots which have been formed by a condensation of sulphur disappear, and the white comes up. Sometimes the stoving is twice repeated if a particularly good white (so-called double-stove white) is required. The goods may also be treated with a solution of soda, in which case sodium bisulphite is formed on the fibre; this process is especially used for straw. Sodium bisulphite is used on the large scale for bleaching loose wool; the wool is steeped for some hours in the solution of sodium bisulphite, and then taken through hydrochloric acid at a hand heat.

Cotton is bleached by steeping in boiling water, which removes all soluble matter. It is then boiled in a solution of soda. After the dressing and grease have thus been removed the cotton is treated with a weak caustic soda-lye, which dissolves away certain resinous matters. The goods are then placed in a clear solution of chloride of lime, which is heated by the admission of steam, and they are then rinsed by a passage

* Sodium bisulphite, known in commerce as leucogene, has some advantages over the fumes of burning brimstone. Its action is more regular and it does not injure the health of the workmen. Liquid sulphurous acid at about 14° Tw. bleaches silk and wool better than the fumes of burning brimstone.—[EDITOR.]

through dilute sours (sulphuric and hydrochloric). The acid is finally removed by an alkaline bath.

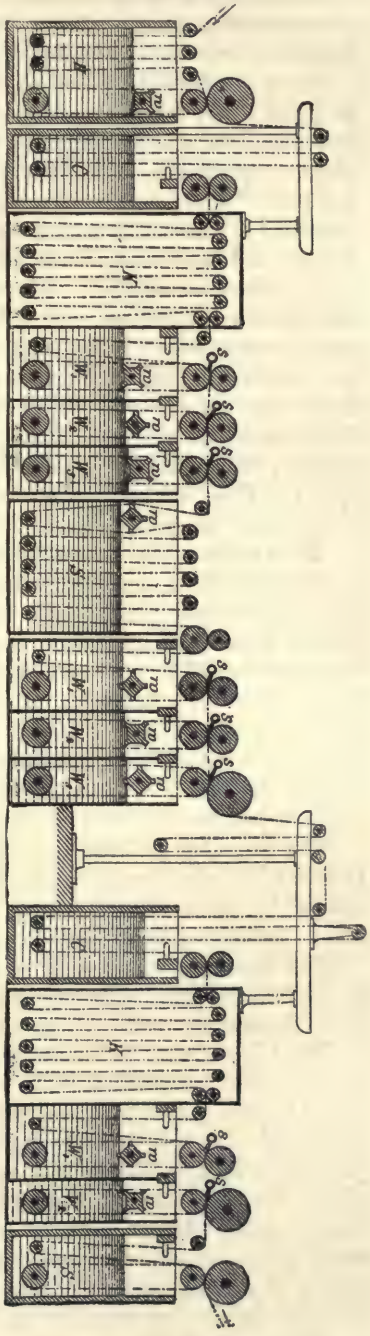
According to H. Koechlin the raw cotton cloth is saturated with alkali and then steamed. The alkali can be used either as caustic, or carbonate, or as soap. The duration of the action of the steam varies according to the concentration of the solution and the pressure of the steam from a few seconds to several hours. As in the ordinary bleaching process, this treatment is preceded by an acid bath and a passage through the solution of a hypochlorite. The cotton, in the state of yarn or cloth, is washed and taken through a bath of dilute hydrochloric and sulphuric acid at 1·0133 sp. gr. It is then allowed to lie wet for one hour and taken through the solution of hypochlorite—preferably sodium hypochlorite—at 1·0066. The cotton is then allowed to lie in heaps for an hour, washed, and passed through soda-lye at 1·0704 sp. gr. It is then steamed for an hour, washed, again taken through a bath of sodium hypochlorite of the above strength, left in heaps for an hour, washed, taken again through a bath of the strength given, again washed and dried.

The bleaching process of J. Thompson is carried out as follows by the firm of Mather and Platt, of Manchester. For removing the dressing the pieces are first taken, spread out, through a solution of soda, for which purpose there is used the washing machine commonly employed in bleach works. They are then laid in basket trucks, simply folded backwards and forwards. These trucks are made of a sheet-iron texture, covered with zinc; they can convey a ton weight of pieces, and run upon rails laid on the floor of the works. The trucks when full are at once run into the new Mather working-pan. This pan is a horizontal cylinder closed at its front by a door, which can be lifted, within which the rails are continued and which has room for two trucks one behind the other. The door hangs from a chain which is conveyed over pulleys to the back of the cylinder and is there joined to a piston to be moved by steam or water-pressure. On admitting the pressure-liquid into its cylinder the door is quickly raised. The steam-tight closure of the door is effected not by means of screw-bolts, &c., but the frame of the door is made wedge-shaped below and the front margin of the boiler is hollowed accordingly, so that the door is tightly closed by its own weight. These arrangements promote speed in loading and unloading. After two trucks full of pieces moistened with the solution of soda have been introduced, steam is turned in at the pressure of 1 atmo. To protect the pieces from the injurious action of dry heat, they are continually moistened with a weak solution of soda, or with caustic lye at 2 per cent. This process is effected by means of a pump which constantly sucks up the liquid from the lowest part of the pan and then squirts it out over the trucks by means of a perforated tube. Instead of the soda-solution hot water is then conveyed into the pan and the goods are washed in the same manner. They are then run out of the cylinder, which immediately receives a fresh charge in the same manner, so that 6 tons of cloth can be prepared daily for bleaching. The trucks with the cloth thus freed from dressing are run to the bleaching machine, into which the pieces are at once transferred, so that there is no interruption in the process.

The continuous bleaching machine of the same firm is an essential requisite for the proper working of the Thompson bleaching process, since by its means the repeated saturation of the tissues with the bleach liquor, the subsequent treatment with gaseous carbonic acid, and the repeated washing, are rendered possible in one passage, whether the pieces are spread out at full width or folded into a cord, in which latter case several such cords can be treated side by side. The pieces move at the rate of about 60 metres per minute. The cloth passes first into the washing beck, *H* (Fig. 562), with hot or cold water, and after being nipped between two rollers it arrives at beck *C*, containing the bleaching liquid (mostly a solution of chloride of lime at 0·4 per cent.). After leaving the nipping-rollers of the beck, *C*, the pieces pass into the carbonic acid

chamber, *K*. This is a simple sheet-iron chest with guide-rollers for the pieces, and provided at the slits left for the entrance and exit of the pieces with slips of caoutchouc, which apply themselves to the cloth and prevent the escape of the gas. The carbonic acid is introduced by a pipe at the bottom of the chest, and a simple arrangement indicates the level of the gas in the chamber, *K*. At one of the sides there is a gas-pipe connected above and below with the interior of the chamber. In the gas-pipe a thin parti-coloured glass bulb, filled with air, indicates the level of the carbonic acid. The carbonic acid, being of a higher specific gravity, keeps the glass bulb suspended at a height corresponding with its own level in the chamber. After the treatment of the pieces with carbonic acid there follows a washing with water and a 0.1 per cent. solution of soda in the several vats W_1, W_2 and W_3, then a passage in a hot solution in *S*, and repeated washing. The beating of the pieces in the washing becks is effected by means of the rollers *w*; the washing water is conveyed upon the cloth between the nipping-rollers through the spirting tube *s*. The goods, conveyed for a little into the open air, arrive for a renewed similar treatment, are washed in the vat *W*, with weak hydrochloric acid, then with water, then with soda-solution and again with water, and are finally conveyed to an ordinary washing machine for the final washing.

Fig. 562.



The advantages of the Mather-Thompson process (with the employment of the plant just described) lie chiefly in the economy of time and washing water. As two pieces can be taken through the apparatus side by side, from 4500 to 5000 kilos., or 36,000 to 40,000 metres, of goods can be bleached in a day of ten working hours. But if we also include the time needed for steaming, it appears that from 2000 to 5000 kilos. (according to the size of the plant) can be completely bleached in eighteen to twenty hours.

The process above described is used for cloth which is to be sold white. But if it is desired to produce good whites for printing the pieces are first taken, not through soda-lye, but through hot sours. The steaming is effected in the same manner, only to 2000 kilos. of cotton there are added 10 kilos. of resin, previously saponified. The chlorinising is effected in the manner above described.

Latterly a bath of weak hydrochloric acid has been substituted for the carbonic acid treatment. For bleaching on the large scale this process seems likely to supersede all others.

Bleaching with chlorine produced electrolytically has been repeatedly attempted but hitherto without noteworthy results.

In bleaching linens, according to Kolb it is necessary to remove two substances, pectic acid and a grey substance formed during the rotting of the flax. This is effected either by the grass bleach or by treatment with chloride of lime. The grey matter is oxidised and the pectic acid is removed in a soluble form.

According to Cross, jute may be easily bleached by treatment with the permanganates and subsequent washing with dilute acids or by means of hydrogen peroxide, but these two processes are too expensive.

Cross washes the cloth with a solution of soluble glass, borax, or soda, at 70° to 80°, and then takes it through a solution of sodium hypochlorite, containing 0·7 to 1 per cent. effective chlorine, corresponding to 2 per cent. chloride of lime. A slight excess of soda completely prevents the formation of chlorinised products from the fibre. After a thorough rinsing the goods are passed into cold, dilute hydrochloric acid, containing a small quantity of sulphurous acid in order to remove salts of iron and basic compounds which might subsequently, in contact with oxidising agents, discolour the fibre. If thus treated the jute has a pale cream colour and a soft, shining appearance. If it is to be dyed it may, after a thorough rinsing, be at once transferred to the dye beck. If intended for printing the pieces are first placed in a bath of sodium bisulphite, containing from 1 to 2 per cent. of sulphurous acid. Here they remain two or three hours and are then dried on steam cylinders. Sulphurous acid escapes and the goods when dry are uniformly saturated with sodium sulphite, which subsequently prevents the oxidising and destructive action of steaming upon the fibre, without interfering with the development of the printed colours. The whiteness of the goods is further improved by the treatment with sodium bisulphite.

If an attempt be made to bleach jute with chloride of lime in the same manner as cotton or linen, a chlorinised compound is formed which is easily recognised by the magenta-red colour which it assumes if moistened with sodium sulphite. If such a tissue were afterwards steamed hydrochloric acid would be set free by the decomposition of the chlorine compounds, a dark brown colour would appear and the tissue would crumble away. Sometimes these changes appear only after the cloth has come into use, which increases the common prejudice against jute. This fibre is further oxidised by hypochlorites to form derivatives which produce insoluble lime compounds. These are deposited on the fibre, so that the common bleaching process converts jute into a rough, brittle, ill-smelling product of low quality.

The first step in bleaching silks is the ungumming. Silk goods which are to remain white are stoved. To mask the yellow tint which remains it receives a slight red tint by means of a solution of annatto in soap-lye, or a blue reflection with aniline blue. Latterly silks are bleached with hydrogen peroxide.

Wool bleaching begins with scouring effected by treatment with stale urine (lant) or with a soap-bath. The bleaching itself is performed with sulphurous acid in the stove, more rarely with sodium bisulphite (leucogene).

Wool intended to be bleached with hydrogen peroxide must be washed clean. If the commercial peroxide is diluted with 10 parts of water the wool should be treated in the bleaching-bath for from thirty to forty minutes. The wool must have sufficient room in the vat to be turned readily, as this expedites the bleaching. If the hydrogen peroxide is diluted with 15 parts of water the wool must be allowed to steep for an hour after it has been taken out of the bleach-bath; the action continues as long as the wool is moist. Hence it should not be dried too rapidly, and if possible it should be dried in the open air with exposure to the sun. If a very dilute peroxide has been used a very small quantity of extract of indigo—which is necessary for the production of a pure white—may be added at once to the bath, and if a more concentrated peroxide bleach is used, the blue tone must be given in a special bath. With strong yellow wools it is well to add to the bath a few drops of dissolved methyl violet.

DYEING AND TISSUE-PRINTING.

Textile fibres are capable of taking up colouring-matters and certain constituents of mordants from solutions and of retaining them. The combination, however, is often so unstable that it is easily destroyed by repeated treatment with solvents, especially with the aid of heat. Thus, a fibre dyed with indigo sulphate, or with Prussian blue dissolved in oxalic acid, can be decolorised by continual washing. The fibre is, therefore, truly dyed only when the dissolved colouring-matter forms with the fibre, and mostly with the co-operation of a third substance, a *mordant*, an insoluble compound which cannot be removed by the application of a solvent. According to Knecht's recent investigations, wool forms with colouring-matters actual chemical compounds. The colour thus produced is called *fast* when it resists the weather, light, soap-lye, dilute alkalies, and very dilute acids. A colour which is destroyed under such circumstances is called fugitive.*

The combination of the fibre with the colouring matter necessary for dyeing may be effected—(1) by *removing the solvent.* Thus, copper oxide dissolved in ammonia can be fixed upon the fibre by the mere evaporation of the ammonia. The precipitation of carthamine from an alkaline solution by means of an acid and the precipitation of many tar-colours soluble in spirit by the addition of water, likewise belong here. An insoluble combination can also be produced—(2) by *oxidation*, the colouring-matter, previously soluble, being rendered insoluble by taking up oxygen. Here belong besides ferrous and manganous sulphate which form insoluble hydrates on oxidation, the tanniferous substances which at the same time contain a colouring-matter, such as quercitron bark, sumach, fustic, fustet, &c. If we saturate cloth with the watery or alkaline extract of these substances and expose it to the air, the colouring-matter is turned brown and ceases to be soluble in water, possibly in consequence of the formation of substances resembling phlobaphene. A similar change is effected more quickly if tissues saturated in this manner are treated with oxidising agents, such as potassium chlorate, chromic acid (alkaline bichromates), or vanadium compounds. An instance of this kind is black-dyeing by means of logwood and potassium chromate, where the hæmatoxyline of the wood is oxidised to hæmateine, and the chromic acid is reduced to a chromium sesquioxide. Similar is blue-dyeing with indigo in the vat and the production of aniline black. Often—(3) the insoluble compound is produced by double decomposition—*e.g.*, blue by a soluble ferrocyanide and ferric oxide, yellow by potassium chromate and a soluble salt of lead. This method of fixation is applicable only with mineral colours. The most important method of fixing colours is—(4) by means of mordants.

Bancroft divided the colouring-matters into substantive and adjective; the former are those which pass into an insoluble state upon the fibre without the intervention of a mordant, as all the mineral colouring-matters, indigo, turmeric, annatto, safflower, and most of the coal-tar colours. By adjective colours he means those which require some mediating agent in order to become insoluble upon the fibre. These mediating substances are the mordants in question. But such mordants have not merely the function of effecting the combination of the colouring-matter with the fibre. They serve in certain cases for effecting such a change in tissues already saturated with earthy or metallic salts that the parts upon which they have been placed appear colourless when lifted out of the flot. Such mordants are called *discharges.* They include the phosphoric, tartaric, oxalic, and arsenious acids. Here also belong the *resists* used in tissue printing. Mordants are often used to modify the tone of colours which have already been produced, rendering them brighter and purer, an effect which is known as *raising* (Fr. *aviviren;* Ger. *schoenen*).

* Compare Leo Vignon, *Chem. News*, vol. lxiii. pp. 153, 177 & 285.—[EDITOR.]

Among the most important mordants are the salts corresponding to the sesquioxides of the general formula, R_2O_3, especially the salts of aluminium, iron, and chrome. Here it is important to present solutions of the salts to the fibre in a form such that they can easily and completely pervade it—with the co-operation of the fibre itself—and to deposit upon the fibre either the oxides or very basic salts. The insoluble compounds of aluminium, iron, chrome, &c., deposited in, upon, or between the several fibres and tufts of fibre form the mordant in the stricter sense of the word. They combine with the colouring matters either chemically, or in the opinion of some, mechanically only, and thus effect the colouration of the fibre, which would otherwise be impracticable. The compounds of antimony are also important.

The chief organic mordants are turkey-red oil (alizarine oil), tannin (especially for fixing the madder colours, cochineal, and the aniline dyes upon cotton and linen), albumen, gluten, caseine, glue, glycerine (sometimes a solution of arsenious acid in glycerine), and fatty oils. The cloth to be dyed is taken through these mordants which are again fixed according to their nature, either by airing, by the dunging process, by the bran bath, or by soaping, and the tissues are then introduced into the solution of colouring-matter.

Alumina mordants were used by the ancients, and are still employed on all kinds of fibres. Aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, is decomposed, according to the researches of Liechti and Suida, by soda or sodium bicarbonate:

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2,$$
$$Al_2(SO_4)_3 + 6NaHCO_3 = Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 3CO_2,$$
$$Al_2(SO_4)_3 + 4NaHCO_3 = Al_2SO_4(OH)_4 + 2Na_2SO_4 + 4CO_2.$$

The more basic the compound the more alumina is deposited upon the fibre. Similar is the behaviour of aluminium acetate, whilst aluminium chloride and aluminium sulphocyanide behave less favourably. Thus, in order—*e.g.*, to mordant cotton it is saturated with a solution of 2 kilos. aluminium sulphate and 0·32 kilo. sodium carbonate in 10 litres of water, diluted if requisite to 1·05 sp. gr., the excess is removed from the cotton by pressure, dried, passed for five or ten minutes through liquid ammonia (0·5 per cent.), washed and dyed. Instead of ammonia there may be used solutions of sodium arseniate or phosphate, soaps, or turkey-red oil.

Aluminium acetates and sulphacetates are especially used in calico-printing. The solutions are thickened with flour, starch, or dextrine, printed upon cotton cloth and dried. Too high a temperature during dyeing must be carefully avoided, especially with mordants which are very readily decomposed (basic salts), as the results will otherwise be uneven and poor. The object is reached by the use of hot plates, hot air, &c., in place of rollers heated by steam. If too strong a heat is employed the mordant fixed upon the fibre is deprived of its water of hydration, or undergoes some physical change by which it is rendered incapable of taking up colouring-matter. When this occurs the printed mordant is said to have been burnt.

Upon printing and dyeing follows ageing, which consists in exposing the printed goods in a more or less open state to an atmosphere at a suitable temperature and degree of moisture. This treatment is rendered continuous by means of the ageing apparatus, a large chamber heated to from 32° to 38°, whilst at the same time steam is admitted until the moistened bulb of the thermometer stands at from 4° to 6° lower. The printed pieces are slowly passed over and under a set of rollers fixed at the top and bottom of the chamber, so that they remain exposed to the moist, warm atmosphere for from twenty to thirty minutes. During this process the starch, or other thickener, is more or less softened by the moisture and the mordant penetrates more completely into the fibre. Quantities of acetic acid are expelled and an insoluble basic salt is fixed upon the cotton. Immediately after leaving the chamber the pieces are rolled up

loosely and left lying to complete the ageing, for twenty-four to forty-eight hours, in a room in which the dry-bulb thermometer indicates 32°, and the wet-bulb 28°.

The next treatment is the so-called "dunging" (Fr. *bousage*, Ger. *kuhkothen*), in which the pieces, spread out, are drawn for two minutes through hot solutions of one or more of the following substances: cow-dung, sodium arseniate, phosphate or silicate, calcium carbonate, &c.

The purpose of dunging is three-fold. Firstly, to retain that part of the mordant which was not affected during ageing more completely upon the fibre; secondly, to protect the unprinted and consequently unmordanted parts of the tissue from the mordants, so that they may not be stained by mordant rubbed off from the printed parts; and, lastly, to remove the thickeners. The last purpose is effected more completely if the dunging is repeated, the pieces being folded up in the form of cords and passed between rollers. The most effective process for removing the thickenings, is to place the pieces for one to two hours in a bran-bath, the diastase of which quickly converts the insoluble starch into soluble glucose. After thorough washing the printed and mordanted cloth is ready for dyeing.

Aluminium acetates (red liquor) are very generally used in many steam colours in calico printing—*e.g.*, in the so-called alizarine steam reds. In the colour or thickened mixture for printing the aluminium acetate is merely mechanically mixed with the alizarine or other colouring-matter; when the printed cloth is exposed to steam decomposition of the mordant takes place, its combination with the colouring-matter and the fixation of the coloured compound upon the fibre also occurring simultaneously.

Experiment shows that pure aluminium acetate does not give such full, rich colours as do double compounds, especially $Al_2SO_4\ (C_2H_3O_2)_3OH$. Aluminium acetates are also used in turkey-red dyeing. For wool dyeing aluminium acetate is unsuitable. Wolf recommends solution of ammonium carbonate for fixing aluminium mordants upon cotton. The use of this agent has the advantage that pure aluminium hydrate, only a small part of which is combined with carbonic acid, is deposited upon the fibre, whilst if we use the ordinary dung-substitutes (substances other than cow-dung used in the dunging process) we obtain basic phosphates, arseniates, &c., the acids of which are much less readily expelled by alizarine or other dye-wares of an acid character; that is, they dye up more slowly.

According to experiments the ammonium carbonate exerts a favourable action especially in the case of mordants containing sulphocyanides, and it is altogether preferable to the use of silicates and ammonia, and equal to sodium phosphate and arseniate. In comparison with the former it has the advantage of producing brighter shades. Ammonium carbonate, other points being equal, is preferable to the arseniate on account of the poisonous character of the latter.

Iron Mordants.—The use of ferrous sulphate (copperas) as a mordant, though still considerable, has been reduced by the introduction of the chrome compounds; the ferrous acetate (black liquor, pyrolignite of iron) is more important, as it serves for blacks, purples, and chocolates; it should be as free as possible from ferric salts.

Iron pyrolignite is especially used for dyeing silks black and for the fraudulent process of "loading" or "weighting." The silk is steeped at 40°–50° in a solution of tannin, especially extract of chestnut, then treated with iron pyrolignite of 1·06 to 1·07 and exposed to the air. This treatment is repeated from twice to fifteen times, and the weight of the silk is increased from 30 to 400 per cent.*

* To counteract the rusty brown tone apt to be thus produced, the silks, after an iron bath (*rouille*) are taken through a solution of potassium ferrocyanide, which produces a deposit of Prussian blue on the fibre. It must be remembered that by the weighting-process silks are not merely rendered liable to a slow decay (*eremacausis*), but they become capable of spontaneous (so-called) combustion.

Ferric sulphate, $Fe_2(SO_4)_3$, erroneously called nitrate of iron, as it is obtained by oxidising copperas with nitric acid, is largely used in silk dyeing, especially in the state of the basic compound: $12FeSO_4 + 3H_2SO_4 + 4HNO_3 = 3Fe_4SO_4)_5(OH_2) + 2H_2O + 4NO$.

In mordanting raw silk it is, according to Hummel, first treated in a solution of sodium carbonate at 40° to 50°, and then worked for half an hour to one hour in a cold solution of the mordant at 14° Tw. The silk is then taken out, well washed, and left to steep for thirty minutes in a solution of sodium carbonate at from 4c° to 50°. It is well washed. These different treatments are repeated three to four times if fraud is intended.

In mordanting boiled silks they are soaked for half to one hour in a cold solution of basic ferric sulphate at 48° Tw., the excess of liquid is removed by pressing, and the silk is well washed, first in cold and then in lukewarm water. This treatment is repeated seven or eight times, and the silk is then put into an old soap-beck at 100°, or in a bath of panama-bark, to which have been added 2 per cent. of soda-crystals, and oleic acid soap equal to about 12 per cent. of the weight of the silk. It is again washed in water when the mordanting process is completed. Both the iron- and the soap-beck remain continuously in use, care being taken to keep up the proper concentration in the former by the addition of fresh mordant, and to boil up a fresh quantity of soap in the latter before mordanting so that the iron-soap which has been formed during former operations may rise to the surface and be skimmed off.

In raw silks where a relatively weak solution of ferric sulphate is used, the gummy matter of the silk occasions decomposition and precipitates a quantity of an insoluble basic salt during dipping. The washing in water and the rinsing in solution of sodium carbonate complete the decomposition and remove the acid salts which have been liberated. In silk which has been boiled off the liquid is simply absorbed by the fibre whilst being dipped into the concentrated solution of the mordant. The use of water containing calcium bicarbonate is advantageous for washing, as it promotes the decomposition of the mordants which have been absorbed. Boiling in soap lye is necessary to complete the decomposition of the mordants, and the temperature of 100° then applied modifies the precipitated ferric sulphate so that it is less easily dissolved in the following baths.

Silk is destroyed by oxidation if it is allowed to lie in the air after saturation with ferric oxide.

Ferric nitrosulphates, so-called nitrates of iron, *e.g.*—

$$6FeSO_4 + 8HNO_3 = 3Fe_2(SO_4)_2(NO_3)_2 + 2NO + 4H_2O$$
$$12FeSO_4 + 10HNO_3 = 3Fe_4(SO_4)_4(NO_3)_2(OH)_2 + 4NO + 2H_2O,$$

are used chiefly for blacks on cotton. Pure ferric nitrate, ferric acetate, and iron-alum are little used.

Nickel mordants, according to Leichti, may be recommended for producing fast colours in light shades. For dyeing the nickel-ammonium chloride, and for printing the nickel nitro-acetate, are to be recommended.

Chrome mordants are of comparatively recent origin. According to Liechti, the quantity of the chromium oxide deposited upon the fibre in mordanting, drying, and ageing increases with the neutralisation, as with the aluminium mordants; in mordants of the same acid, of the same degree of neutralisation but different production, the presence of foreign salts has an unfavourable influence. Alkaline sulphates especially, under circumstances otherwise the same, decrease the quantity of the chromium oxide retained by the fibre, and must be considered as agents which retard dissociation. The fixation of the acetates and mixed acetates during drying, &c., is, with the exception of those mordants which incline to spontaneous decomposition, to be referred alone to the decomposing influence of the fibre, as in the absence of the fibre insoluble basic salts are not obtained by the evaporation of acetic acid. The strongly basic

sulphates, $Cr_2(SO_4)_2(OH)_2$, $Cr(SO)_4(OH)_6$, $Cr_2SO_4(OH)_4$, &c., yield the largest quantity of chromium oxide to the fibre, but never in so large a proportion as in the case of certain aluminium products. Kopp recommends chromium fluoride.

Chromium chlorate is recommended by Lauber, and H. Koechlin proposes a mixture of 16 parts solution of chromium acetate at 24° Tw., 48 parts water, 32 parts soda-lye at 66° Tw., and 1 part glycerine. After mordanting, the goods are allowed to dry for some hours and are then washed. The more caustic the solution of chrome the better it acts; if the proportion of soda-lye is insufficient, little or no chromic oxide is deposited on the fibre. On the other hand, if the causticity is excessive the fibre contracts strongly. According to Schmidt, this phenomenon always takes place, and in moderation it is not unwelcome, since it strengthens the fibre by mercerisation. Alkaline chrome mordants must be used with care, as they may produce sores. If cotton yarns are mordanted by hand, caoutchouc gloves should be used. Instead of fixing chromium oxide by letting the cloth lie for some time rolled up, the same end is reached in a very short time by steaming. Knecht shows that the quantity of chrome deposited upon wool varies with the concentration of the solution. If we take the quantity of chrome precipitated upon the fibre as a measure for the efficiency of the mordant, chromic acid is by far the best chrome mordant for wool. Next in value follows potassium dichromate along with sulphuric acid, then the dichromate alone, and, lastly, neutral potassium chromate.

*Tin Mordants.**—Stannous chloride, $SnCl_2 2H_2O$, called salts of tin or tin crystals, is still extensively used in printing, both as a solid and in solution. Generally the stannous salts are more serviceable for woollens and the stannic salts for cotton goods. Sometimes stannous chloride is added to the dye-bath towards the end of the dyeing process, in order to heighten the shade. Stannic chloride, and less frequently "pink salt," $SnCl_4(NH_4Cl)_2$, as well as sodium stannate, have a number of applications.

Manganese Mordants ($MnCl_2$ and $KMnO_4$) and lead mordants are little used, the affinity of lead for the fibre being feeble. Copper mordants, especially the nitrates, $Cu(NO_3)_2$, are sometimes used on account of their oxidising action—*e.g.*, in catechu colours.

Antimony Mordants were first recommended by Brooks, in order to combine tannin at once with colouring matter and with a metallic oxide, which he effected with tartar emetic, $K.SbO.C_4H_4O_6$. The action of all antimonial mordants depends on the fact that antimony oxide deposits on the fibre as an antimonial lake in conjunction with tannin, thus fixing the colour upon the fibre.

On account of the high price of tartar emetic, potassium-antimony oxalate has latterly come into use. Koehler recommends antimony oxide in an alkaline solution of glycerine as a mordant for cotton dyeing. Antimonious chloride and antimony lactate have been recommended. Of more importance is the antimony sodium fluoride, $SbNaF_4$, and especially ammonium antimony fluoride sulphate, $SbF_3(NH_4)_2SO_4$.

Tannin Mordants.—For colours of a basic character, such as magenta, malachite green, &c., tannin plays the part of a mordant, just as does alumina for alizarine, as it combines with the colourless base contained in these colouring-matters and produces an insoluble lake. During the precipitation of a basic colouring-matter from its solution by means of tannin, the acid previously combined with the colour base is liberated. J. Koechlin has remarked that the addition to the mixture of an alkali like sodium carbonate makes the precipitation easier and more complete. For the production of a tannin lake it is, according to Hummel, not necessary that the tannic acid should be

* The importance of the tin mordants has greatly declined since the introduction of the coal-tar colours. So long as scarlets, crimsons, and other bright colours had to be obtained from cochineal, lac and the woods, compounds of tin were used in a multitude of modifications, and much skill and nicety were needed in their preparation.—[EDITOR.]

in a free state. Insoluble metallic tannates have as great, if not a greater, affinity for basic colouring-matter. The presence of the metallic oxide facilitates the decomposition, because it neutralises a part of the liberated acid of the colouring-matter, and there is probably formed an insoluble bibasic compound (antimony and colour-base tannate). But the use of insoluble metallic salts prevents the lake formed upon the fibre from re-dissolving, either on account of an excess of tannin or of colouring matter. An excess of tannin yields soluble compounds with basic colouring-matters, so that the exact amount of tannin needful must first be deposited upon the fibre and then the colouring-matter.

Tannin forms insoluble compounds with alumina and the iron, tin, and antimony oxides. These bases act as mordants for colouring-matters of an acid character, whether they occur as hydrates or in combination with tannic acid or other acids, such as the phosphoric, arsenic acids, &c. They have still the power to attract such colouring-matters, and to form with them coloured lakes. For this reason tannin is often used as a precipitant or fixing agent for aluminous, tin, or iron mordants.

The tannin compounds obtained with the iron mordants have a bluish black colour, of sufficient intensity to serve as a grey or even as a black dye. In this respect tannin may be regarded as a colouring-matter in the same manner as alizarine. In many cases the blue-black iron tannate serves merely to darken certain colours, which is effected by means of preparations specially applied. In such cases the iron tannate acts at once as a mordant and a ground colour.

Cotton is worked, or steeped in a solution of tannin, and the excess of liquid is removed by draining or nipping, sometimes followed by drying. In padding, the cotton is saturated with the solution for a few seconds, and is then wrung out and dried. In this case the solution employed must contain at least ten times as much tannin as the former process, if it is to be equally effective.

If textile fabrics soaked in oil—especially castor-oil or olive-oil—are exposed to the air, the oil is partially decomposed, and the free fatty acid forms insoluble soaps with the aluminous mordants. Especially important is the turkey-red oil obtained by treating these oils with sulphuric acid, on the composition of which there is still a variety of opinions. Its chief constituent is probably (according to Benedikt) sulphoricinoleic acid, $C_{18}H_{33}O_2.OSO_3H$. It is used in turkey-red dyeing, and in fixing aniline colours upon the fibre.

The rancid smell of tissues mordanted with oil is unpleasant.

Albumen and casein (dissolved in ammonia or borax) and gelatine are used in tissue printing.

Apparatus.—Of the recent apparatus used in dye-works the following may be mentioned:—

Colour-pans for Laboratories are heated by steam, according to Dawson's design. In a strong cast-iron tray, *M* (Figs. 563 and 564), fixed in a frame so as to admit of

Fig. 563.

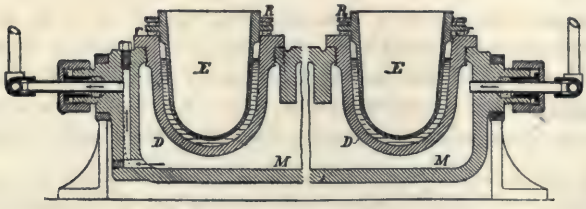
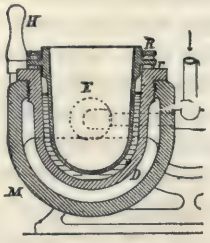


Fig. 564.



turning, the cast-iron pans, *D*, are fixed steam-tight by means of screws. The pans, *D*, receive water used for a water-bath, or preferably in its place glycerine, into which the

copper dye-pan, *E*, is fitted and secured by the brass ring, *R*, and the caoutchouc rings, *r*. The lower ring prevents the escape of annoying vapours from the liquid bath. Into the tray, *M*, steam of about 4 centimetres is admitted at one side through the revolving plug, whilst the condensed water escapes from the lowest point of the tray by a vertical channel. Handles, *H*, allow the entire series of pans to be emptied by turning the tray, *M*. To prevent felting, loose wool and cotton are exposed to the rotating liquid in a compressed state.

Fig. 565.

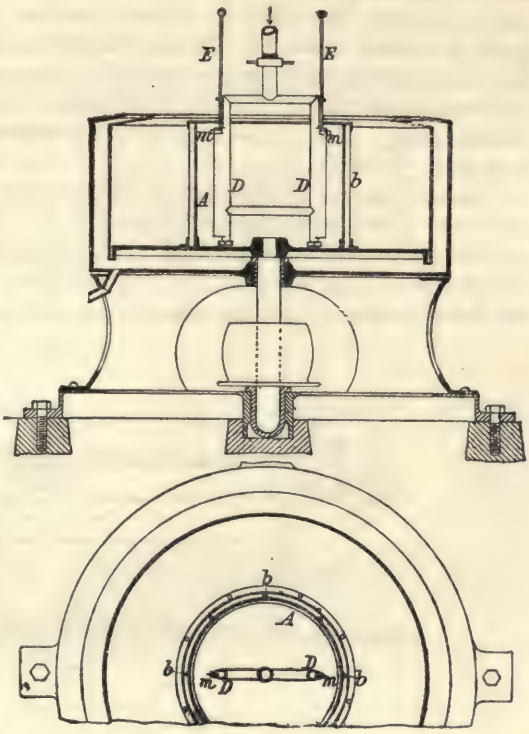
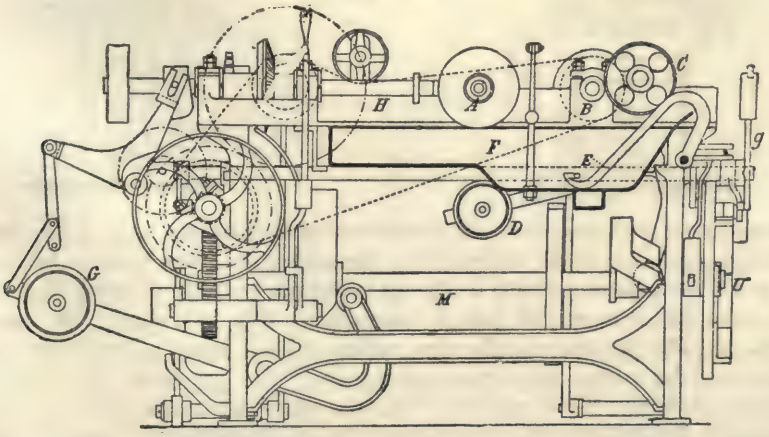


Fig. 566.

For bleaching and dyeing cops O. Fisher recommends a centrifugal machine. Into the internal sieve, *A* (Figs. 565 and 566), there extend the two tubes, *D*, fed in common by one conductor, and both having a slit, through which the liquid issues uniformly, in its entire height. In order to cleanse the slits there are small slides, *m*, fixed to the rods, *E*, and dirt may thereby be expelled from the machine even while it is at work. The tubes, *D*, are also closed below with nuts provided with holes, so that dirt cannot accumulate or can be easily removed by unscrewing the nuts.

For the uniform saturation of the yarns with dye liquor, mordants, or dressing, &c., there are used, especially in indigo and turkey-red dyeing, so-called passing-machines,

Fig. 567.



the general arrangement of which is shown in Fig. 567. First the roller *A*, fixed perpendicularly on the axle *H*, is pushed up to roller *B*, so that a workman can easily hang the yarns over *A* and *B*. The nipping roller, *C*, fixed on the weighted lever, *D*,

presses against the roller, *B*, the lever, *E*, which stands above the roller, *B*, falls down into the position shown, and draws the yarns into the bath in the cistern, *F*; so that when the roller, *B*, is turned, they are carried along through the beck. After a certain time the yarns are stretched, the axle, *H*, being brought back by the weight, *C*; the roller, *C*, and the lever, *H*, return to their original position, and the axle, *H*, revolves, whereby the yarns are wrung out. The axle, *H*, then in turning back wrings the yarns again, the roller, *B*, makes a rotation, and the axle, *H*, wrings the yarns again by moving forwards. This is twice repeated, so that the parts which lie over the rollers may be uniformly wrung out. The weight, *G*, is then lifted off, and the machine stands still to allow the dyed hanks to be taken off, and fresh ones to be put in their place. The introduction of these various movements is effected by curved discs from the shaft, *M*.

The machine for dyeing piece-goods and yarns, made by the Zittau Machine Works, consists of a trough for the flot (Figs. 568–571), over which there are several reels, *B*, movable alternately from the right to the left, and reversely over the entire length of the trough, or a portion of it, and keeping all the time in rotation. By this slow to and fro and alternately turning movement of the reels the pieces to be dyed are moved

Fig. 568.

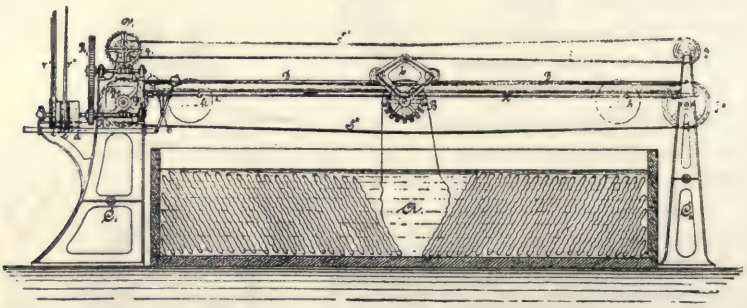


Fig. 569.

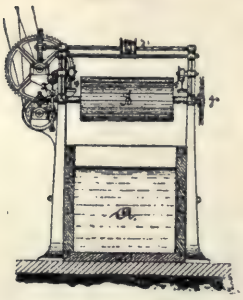
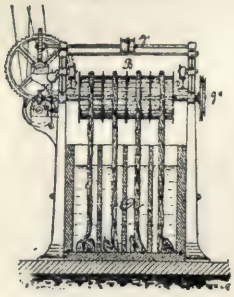


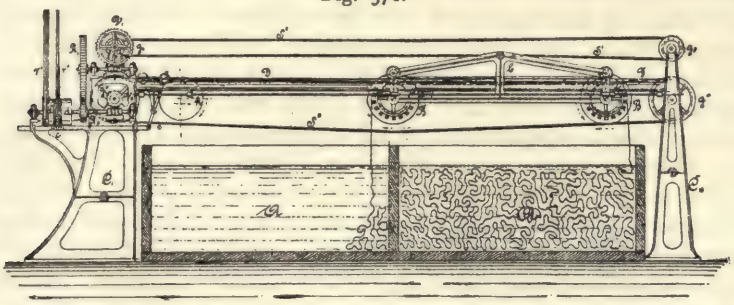
Fig. 570.



in such a manner that the pieces are always conveyed from one half of the trough to the other in quite even folds, and are thus brought in uniform contact with the dye liquor, and it is rendered possible to dye up any given quantity of goods at once in one and the same flot, or in several flots in succession. Fig. 568 shows the machine in elevation, and Fig. 569 gives a side view, with a smooth drum, and with an undivided trough as used for dyeing piece-goods, spread out. Fig. 570 shows the elevation, and Fig. 571 the side view of the machine, with two compartments provided with reels, and with a trough divided into two compartments in length and four in breadth, as applied for yarns in warps (French, *chaines*; German, *Ketten*), and for pieces folded up. In both cases the reels are placed capable of rotation on rolling trucks, *b*, which run on horizontal rails, *D*, fixed to the supports, C_I C_{II}. The movement of these trucks to and

fro, and the alternatin rotatory movement of the reels, B, is effected by the endless band, S″ S″, which in turn is moved by the screw wheels, $V_{,}$ $V_{,,}$, or the band discs, g' g'', fixed on the shafts of the screw wheels. The screw-wheel shafts, $V_{,}$ $V_{,,}$, are connected by the wheels, $R_{,}$ $R_{,,}$, with a corresponding number of teeth, according as the open band, r', or the cross band, r'', runs upon the middle disc, c, whilst each

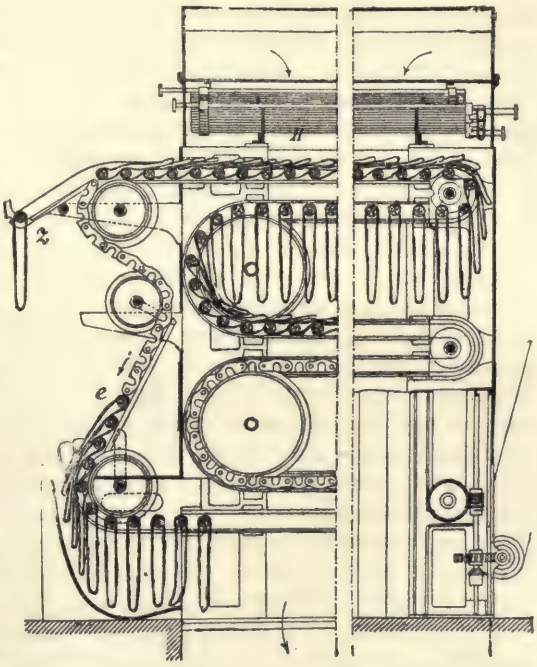
Fig. 571.



time the other band runs upon one of the discs d. The change effected thereby is that the rail, K, is pushed to the left or to the right by the impact of the truck, b.

In Sulzer's yarn-dyeing machine the yarns are exposed to a current of hot air alternately in a freely suspended and in a horizontal position, and arrive progressively at higher temperatures as the dyeing proceeds. The hanks of yarn are suspended on rods at e, which, as appears from Fig. 572, are laid in endless chains moving backwards and forwards. Similar is the yarn-dyeing machine constructed by the Hartmann Machine Works at Chemnitz. The difference between the Sulzer and the Hartmann machine lies in the management of the chains and the arrangement of the system of hot-air pipes. The temperature of the current of air, which is 60° above, falls to 30° at the exit from the machine. A drying machine 5 metres in length, $3\frac{1}{2}$ metres wide, and 4 metres high, dries in eleven hours 1300 to 1400 kilos. of yarn, and requires about 4 horse-power.

Fig. 572.



Dyeing Woollens.—Wool is dyed either loose or spun into yarns, or after weaving as cloth. As in working up the wool a certain part is always lost in the mechanical operations, piece-dyeing is the most advantageous.*

Blue Dyeing.—The imparting of a blue colour to wool is one of the most important

* On the other hand, it is the most difficult. Any unevenness in dyed wool or yarn is lost afterwards, but a spot on a woven piece is a permanent defect. If the colour to be produced is required to be fast, the cloths are often prepared by boiling in solutions of alum and tartar, of copperas and tartar, or of tartar and stannic chloride, or pink salt. All processes which involve the use of tartar (argol) are expensive, and it is therefore dispensed with whenever possible.—[EDITOR.]

operations of dyeing woollen goods. It is frequently effected with indigo, which produces the most beautiful and fast colours; but indigo is used only for the better and heavier kinds of woollen fabrics; lighter tissues—merinos, for instance—are often dyed with Prussian blue (not a fast colour), while common woollen goods, flannels, &c., if dyed blue at all, are dyed with logwood and blue vitriol (copper sulphate). In order to ascertain whether a woollen tissue has been dyed with indigo, Prussian blue, or copper salts, the following tests may be employed. Woollen tissue dyed with indigo does not change its colour by being boiled with caustic potash, or by being moistened with concentrated sulphuric acid. When Prussian blue is the dye used, the tissue becomes red-coloured by being boiled with caustic potash, and becomes discoloured by being moistened with strong sulphuric acid. Woollen goods dyed with logwood and copper salts are reddened by being moistened with dilute sulphuric acid, and, on being incinerated, the tissue leaves an ash containing copper.

Indigo Blue.—Woollen goods are most frequently dyed blue with indigo by means of a solution of white indigo (reduced indigo) in an alkaline fluid, the goods being blued by exposure to air—that is to say, by the oxidation of the indigo taken up by the fibre, the dye becoming simultaneously fixed. The principle of this mode of dyeing with indigo (technically known as blue vat) may be elucidated by the following formula:—$C_{16}H_{12}N_2O_2 + O = C_{16}H_{10}N_2O_2 + H_2O$.

Blue Vats.—The greatest consumption of indigo is in forming the blue vats, in which woollen or cotton goods, more rarely linen, are dyed by simply immersing them in the solution of white indigo. The same vats are not equally adapted for wool and calico, there being, as will be seen in the following details, a wide difference in their composition. According to the general accounts, the lime and copperas vat (see below) is not well adapted for woollen goods; still, in the most recently published French treatise on woollen dyeing there is no mention made of any other kind of vat; the following proportions and directions being given for setting a vat for dark blue:—1200 gallons of water; 34 lbs. of quicklime; 22 lbs. of green copperas; 12 lbs. of ground indigo; 4 quarts of caustic potash solution at 34° = sp. gr. 1·288. The indigo is ground very fine by trituration in properly constructed mills, this being a point of the utmost importance. In the above recipe the potash is mixed with 5 gallons of water in an iron pan, and the indigo added. The mixture is gradually heated to ebullition and kept boiling for two hours with uninterrupted stirring; this softens and prepares the indigo for dissolving. The lime is well slacked so as to be very fine, and is next passed through a sieve in the state of milk of lime. It is then mixed with the indigo and potash; the copperas (ferrous sulphate), previously dissolved, is added to the vat and well stirred; then the mixture of lime, potash, and indigo is poured in, and the whole well stirred for half an hour. If the proportions are well kept, the vat will be fit for working in twelve hours; if, however, it looks blue under the scum, it is a sign that the indigo is not wholly dissolved, and more lime and copperas should be added, and the vat left undisturbed for another twelve hours. The vat is worked at a temperature of 70° to 80° F. This is the ordinary composition of a vat for dyeing cotton, but is not, at least in England, in use for dyeing woollen goods.

The usual blue vats for wool contain neither copperas nor lime, or but a small quantity of the latter; as, for instance—Water, 500 gallons; indigo, 20 lbs.; potash (carbonate, pearl-ash), 30 lbs.; bran, 9 lbs.; madder, 9 lbs. The water is heated to just below its boiling-point; the potash, bran, and madder are first put into the vat, a well-made wooden tub of convenient size, and then the indigo, previously very finely ground. Cold water is added so as to reduce the temperature to 90° F., and that temperature is maintained constant by means of a steam-pipe. The ingredients are well stirred every twelve hours. The vat is generally ready for use in forty-eight hours after setting. This vat does not work longer than about a month, and is somewhat

expensive on account of the potash. Another—the so-called German—vat is much more manageable, and may be worked for two years without emptying, being freshened up as required. It is composed of the following ingredients:—2000 gallons of water are heated to 130° F., and there are added 20 lbs. of crystals of soda (common carbonate); 2½ pecks of bran; and 12 lbs. of indigo, the mixture being well stirred. In twelve hours fermentation sets in; bubbles of gas rise; the liquid has a sweet smell, and has assumed a green colour; 2 lbs. of slaked lime are now added and well stirred, the vat is again heated and covered up for twelve hours, when a similar quantity of bran, indigo, and soda, with some lime, is added. In about forty-eight hours the vat may be worked; but as the reducing powers of the bran are somewhat feeble, an addition of 6 lbs. of molasses is made. If the fermentation becomes too active, it is repressed by the addition of lime; if too sluggish, it is stimulated by the addition of bran and molasses. Like all the other blue vats for wool, it is worked hot. Another kind of vat may be called the woad vat, because a considerable quantity of woad is added to it, and also madder, which in this case acts simply by reason of the saccharine matter it contains. The proportions are:—Pulverised indigo, 1 lb.; madder, 4 lbs.; slaked lime, 7 lbs., boiled together with water and poured upon the woad in the vat. After a few hours fermentation sets in, and fresh indigo is added according to the depth of colour required to be dyed. The pastel vat is set with a variety of woad which grows in France, and which is richer in colouring matter than the common woad. It is possible that the colouring matter of the pastel adds to the effect; but it is more likely that, while it furnishes fermentiscible matters useful in promoting the solution of indigo, it is added as a remnant of ancient usage. Before indigo became again known in Europe (the dye was known to the Greeks and Romans) in the seventeenth century, woad was the general blue dye material. The method of dyeing the woollen fibre and fabrics is very simple. The wool, thoroughly wetted out, is suspended on frames, and dipped in the vat for an hour and a half or two hours, being agitated all the time to insure regularity of colouring. The pieces are then removed, washed in water, and treated with weak hydrochloric or sulphuric acid to remove the alkali retained. As regards blue vat for cotton dyeing, in some exceptional cases, when thick and heavy goods have to be dyed, the so-called German vat is used; but generally all calicoes are dyed blue by means of the cold lime and copperas vat. The materials used are lime, ferrous sulphate, ground indigo, and water. The chemical action consists, in the first instance, in the formation of calcium sulphate and ferrous oxide; the latter substance, having a considerable affinity for oxygen, removes an atom of it from the blue indigo, converting it into white, which dissolves in the excess of lime, and is ready for dyeing. The proportions are as follows:—900 gallons of water, 60 lbs. of green copperas, 36 lbs. of ground indigo, and 80 to 90 lbs. of slaked lime. These are stirred up together every half-hour for three or four hours, then left twelve hours to settle, well raked up again, and as soon as the vat has subsided it is ready for dyeing.

The urine vat is set up by dissolving indigo in stale urine (lant). The indigo is reduced by the organic matters of the putrescent urine, and the indigo-white thus obtained dissolves in the ammonium carbonate produced at the same time. This vat is difficult to manage, and is rarely used either for wool or cotton.

The hydrosulphurous vat (of Schutzenberger) is set up by bringing a concentrated solution of sodium bisulphite in contact with zinc powder. The zinc dissolves without any escape of hydrogen, and a hyposulphite is formed: $SO_2 + Zn = ZnSO_2$. The zinc oxide is eliminated by an addition of milk of lime. This liquid is filtered with exclusion of air and mixed with ground indigo and soda or hydrate of lime, when a solution of indigo-white is quickly obtained. This vat is suitable either for animal or vegetable fibres, and is less liable to "diseases" than the fermentation vats.

The arsenical or orpiment vat is more used in tissue-printing than in dyeing blue on woollens. It is set by dissolving orpiment (As_2S_3) and indigo in potassa-lye, and the solution is thickened with gum and printed.

In the tin vat, indigo is brought in contact with a solution of stannous oxide in caustic potassa, or caustic soda is boiled with indigo and metallic tin. There is a formation of indigo-white and an alkaline stannate. This vat is chiefly used in tissue-printing.

Saxony Blue.—As already stated, indigo dissolves in concentrated sulphuric acid, forming (because it is not a solution in the ordinary sense of the word) sulphindigotic acid, which is employed in dyeing wool in the following manner:—First, 1 part of indigo is treated with 4 to 5 parts of fuming sulphuric acid; next, this solution is poured into a vessel containing water; and into this mixture flock wool is immersed for twenty-four hours. After this time the wool is removed from the vessel and drained, and transferred to a cauldron filled with water, to which has been added either carbonate of ammonia, or of soda, or of potash, and boiled for some time. The solution thus obtained, technically known as extract of indigo or as indigo carmine, is used for dyeing wool which has been previously mordanted with alum. There is formed on the wool aluminium sulphindigotate.

Recovery of Indigo from Rags.—In order to recover the indigo from scraps and rags of woollen and other fabrics dyed indigo blue, the materials are treated with dilute sulphuric acid, which is heated to 100°. The wool is dissolved, while the indigo is left as an insoluble sediment. Military uniforms yield from 2 to 3 per cent. of indigo. The acid solution is next neutralised with chalk, and a calcium sulphate is obtained which, owing to the nitrogenous matter intermingled, may be usefully employed as a manure.

*Berlin Blue, Royal Blue.**—Wool is dyed with the so-called Prussian blue (iron ferrocyanide) by two methods, one of which consists in saturating the wool with a solution of a ferric salt (generally the persulphate, or preferably the pernitrate), after which the wool is passed through a solution of potassium ferrocyanide in water, acidulated with sulphuric acid. The other process, producing the so-called *Bleu de France*, is based upon the decomposing action which the atmosphere exerts on the ferro- and ferricyanhydric acids. The goods are immersed in a solution of either the ferro- (yellow) or ferri- (ruby-red) potassium cyanide (commonly called yellow or red prussiate) in water, to which are added sulphuric acid and alum. Afterwards the goods are aged, or exposed to the air in rooms in which steam is simultaneously admitted to elevate the temperature and assist the action of the oxygen of the air. The result is that the ferro- or ferricyanhydric acid is decomposed, hydrocyanic acid being evolved, while there is deposited on the fibres of the woven fabric iron ferrocyanide, Prussian or Berlin blue. Meitzendorff has proposed a method of dyeing this blue by which a colour is produced very similar to that obtained by the so-called Saxony blue. He prepares a solution containing potassium ferrocyanide, stannic chloride ($SnCl_4$), tartaric and oxalic acids; this solution is heated, and the wool kept therein for some time. The oxalic acid dissolves the Prussian blue, which of course can only act

* This colour is called in Germany "kali blue," which is confusing, as the name "alkali blue" is there given to Nicholson blue. The first method given above for producing Berlin blue on wool is not satisfactory. The best royal blue, on 36 lbs. wool, is obtained as follows:—Mix 4 lbs. potassium ferrocyanide and 6 lbs. oxalic acid; dissolve, enter wool at 100° F., and work well for two hours, raising heat gradually to 180° F.; take out, and cool. Cool liquor with 2 pails cold water; add 21 lbs. alum, and work for half an hour. Add ¾ pint "yellow spirit," and work for one hour, raising heat to 180° F., at which heat work for an hour and a quarter longer. Take out, and add 1 to 2 pints nitrate of iron, according to shade required. Enter wool, and give five or six turns. Take out, cool, and wash very well. This is an expensive colour, and is generally superseded by aniline blues.—[EDITOR.]

as a dye when dissolved, any of it left undissolved being lost. The tartaric acid increases the brilliancy of the colour.

Logwood and Copperas Blues.—For this purpose logwood is boiled in the dye-beck with water, and to the decoction are added alum, cream of tartar, and copper sulphate. The wool is boiled in this fluid, and is next cleared by being boiled in a fluid containing logwood, tin salt (stannous chloride), alum, and cream of tartar. The goods dyed in this manner do not, as is the case with the indigo goods, become white by wear. Instead of logwood, archil and cudbear are frequently used for so-called half-fast colours.

In dyeing blues on wool with coal-tar colours the chief dyes employed are Nicholson blue and methylene blue; blue-blacks are obtained with the indulines.

For dyeing with indophenol wool, silk, or cotton mordanted for turkey-red, the following mixture is prepared:—10 litres acetic acid, 10 litres tin acetate, 2 kilos. indophenol, 5 litres calcium acetate at 27° Tw., and 1 litre black liquor at 14° Tw. The whole is heated to effect reduction, and poured into 500 litres of water. The pieces are worked in this flot at 60° for two hours, washed and oxidised with bichromate. If the wool has been slightly chlorised, it dyes up more readily and gives a deeper blue, which bears soaping at a boil much better. According to Rosenstiehl's proposal the wool may be dyed in an alkaline bath. It is plunged at 50° for two minutes into 1 litre water, 200 grammes soda crystals, 25 grammes indophenol, and the same weight of glucose; it is then exposed to the air for some minutes, and the blue is fully developed by chroming.

For dyeing with alizarine blue (S), which in many cases threatens to supersede indigo, the wool is mordanted with chrome by boiling with 3 kilos. potassium bichromate and 2½ kilos. argol to 100 kilos. wool. For light shades it is sufficient to boil for one hour with 2 per cent. potassium bichromate and 1 per cent. argol. If the water contains lime it must be corrected with acetic acid. The wool is well turned in the dye-beck until the liquid is clear. The process must be continued at a boil until the colour, which at first appeared reddish, takes a pure blue tone.

Dyeing Yellows.—On the Continent, weld, which has become quite obsolete for dyeing yellow on wool in the United Kingdom, having been entirely superseded by quercitron bark, is still used for producing a yellow dye, on account of the fact that weld, when brought into contact with an alkali, becomes less red-coloured than do the other yellow dyes.

In dyeing with weld its colouring-matter is extracted by water, and the decoction added to the goods intended to be dyed. With alum it dyes a very fine clear yellow, tolerably permanent in soap, but not resisting air and light. Weld has not more than one-fourth the tinctorial power of quercitron bark, and on this account, as well as on that of its great bulk relative to its weight, it is not used in this country. Fustic, yellow-wood, is very extensively employed in dyeing, and is the most suitable yellow matter for working with other colours in compound shades. With aluminous mordants it gives yellow of an orange shade; with iron mordants it gives drabs, greys, and olives. As a yellow colouring-matter it is considered to be weight for weight of far less power than quercitron bark, while it is also inferior in purity of colour; but as fustic withstands the action of acids and acid salts better than bark, it is used in greens, blacks, and mixed colours where yellow is required. Young or French fustic (also known as *Venice sumac* or fustet) is used for imparting yellow to merinos. A golden yellow is produced upon wool with either picric acid or Manchester yellow.

Martius's yellow, Victoria orange, aurantia, chrysoidine, tropæoline, &c., have to a great extent superseded the vegetable yellows.

Red Dyeing.—Cochineal and lac are the chief colouring matters used for giving wools a red or scarlet colour. The goods are prepared by boiling in a bath of cochineal, tartar,

and tin crystals or scarlet spirit, and finished with cochineal and scarlet finishing spirit, a stannous chloride to which much oxalic acid has been added.* For crimsons a part or the whole of the cochineal used must be previously prepared with ammonia. The water used should be pure and soft, and especially free from even the least trace of iron.

Faster, though less brilliant, reds are obtained with madder, or latterly with alizarine. The goods are prepared by boiling with alum and tartar, and then dyed with alizarine.

The redder azo-colours have very much interfered with the use of cochineal.

Roccelline, a colour obtained by diazotising naphthylaminesulpho acid and conjugating with β-naphthol, has to a great extent displaced orchil, and in some cases it is even used in place of cochineal and madder. It is very extensively employed for silk-dyeing, which is done in a curdled soap-beck, the colour being afterwards raised with sulphuric acid. For wool-dyeing Roussel acidifies the beck slightly with hydrochloric acid, heats to 50°, and lets the wool steep for from fifteen to thirty minutes. The roccelline is gradually added, and the temperature is then gradually raised to 90°, at which point it is allowed to remain for half an hour. By the addition of chrysoine a colour is obtained which may be substituted for madder-reds. Other tones are produced by mixtures of roccelline with extract of indigo, chrysoine orange, naphthol yellow, &c. The extract of indigo is added towards the end of the process, along with sulphuric acid and Glauber's salt. These colours prove, on exposure to air, almost as fast as cochineal, and more permanent than orchil. Their tone is also unaffected by acids and alkalies. The production of roccelline shades is cheaper by 80 per cent. than those produced with cochineal, and by 40 per cent. than those obtained with orchil.

Green Dyeing.—Green dyes are usually obtained by combining blue and yellow. Wool is first dyed blue, and, having then been mordanted with cream of tartar and alum, is dyed with fustic, or, on the Continent, with weld. The green cloth used for covering billiard-tables and other furniture is dyed in the following manner:—A weak decoction of fustic is prepared, and into this some Saxony blue is poured, while there is next added alum and cream of tartar. The woollen fabric is immersed in the bath and boiled for two hours. It is next thoroughly washed and brightened by being again immersed in a dye-beck filled with a fresh fustic decoction, to which a smaller quantity of Saxony blue has been added. All kinds of woollen tissues, worsted, half-wool, alpacas, delaines, &c., may be dyed green by means of lo-kao (Chinese green) and iodine green.

Among the green tar colours those most commonly used are methyl green, malachite green, and iodine green. As methyl green is transformed at high temperatures into a violet colour, hot rollers cannot be used in finishing goods dyed with this colouring matter. Malachite green and analogous tar colours are often used along with picric acid. Mixed colours, singularly spoken of in France and Germany as *modes*, are obtained by mixtures of greens with cochineal, fustet, madder, &c.

Black Dyeing.—Excepting only aniline black, all black dyes may be considered as combinations of iron or chrome with tannic or gallic acid; but the best and fastest blacks on broadcloth are such as have as a first dye either madder or indigo. The woollen goods are mordanted with ferrous sulphate (green copperas) and dyed by immersion in a decoction of logwood, galls, sumac, &c. The so-called Sedan black (this town is celebrated for its cloth manufacture) is produced by dyeing the cloth blue with woad, when, after careful washing, it is placed in a dye-beck containing water, sumac, and logwood, and is boiled for some three hours, after which copperas in a solution of known strength is added. This operation is repeated until the cloth has assumed an intensely black colour. Half-fast black colours are produced on cloth by dyeing

* The composition of the bath requires to be varied according as the wool is hard or soft; some dyers use a stannic chloride.—[EDITOR.]

them blue with Prussian blue, after which the operation just described is gone through. Common black is produced by dyeing with logwood, sumac, some fustic, and a mixture of green and blue vitriol. Chromium black, invented by Leykauf at Nüremberg, is obtained in the following manner:—The cloth is mordanted with a solution of potassium bichromate and cream of tartar, after which it is dyed in a decoction of logwood. The so-called iron pyrolignite (crude iron acetate prepared from scraps of old iron and crude acetic acid) is now very generally used as a mordant instead of the green copperas. This acetate, also known as black or iron liquor, is prepared on the large scale and sold as a liquid at a sp. gr. of 1·09 to 1·14.

Vienna black, used in the cloth works in the Department Isère, is obtained as follows:—For one piece of cloth weighing 30 kilos. there are boiled in the dye-pan 6 kilos. logwood and 1 kilo. fustic for thirty minutes; 2 kilos. gall-nuts are added, and as much sumac, and it is again boiled for half an hour. The cloth is then entered and turned for half an hour, taken out, and aired. 2 kilos. of copperas are dissolved in the beck, and the cloth is again entered and worked for one hour, without coming to a boil. It is again taken out, 1 kilo. of copperas is added, and the cloth is re-entered and again treated as above. Finally, it is washed in a fulling mill.

Very similar is the Bedarieux black produced upon woollens in a boiling bath of logwood (3 kilos. to 15 kilos. cloth), 0·5 kilo. fustic, and 3 kilos. sumac, with the addition of 0·75 kilo. copperas.

Geneva black is obtained with logwood and fustic, with copperas and bluestone along with a little argol.

Tours black is got up with logwood, sumac, copperas, and a little verdigris. The cloth is entered five times in the dye-bath and aired between each operation, whence it is called *noir à cinq feux*.

Nenuphar black is obtained by boiling wool with the roots of the white water-lily, logwood, and a little sulphuric acid, and dyeing up, after airing, with copperas or black liquor.

Vanadium black on wool is an aniline black obtained in a flot of 1000 water, 80 salt of aniline, 40 potassium chlorate, 5 hydrochloric acid, and 0·1 ammonium vanadate. That cloth dyed black is especially liable to become rotten is due on the one hand to the oxidising action of the iron mordants, and on the other to the circumstance that when the dyer has failed in producing the right shade on a piece of cloth it is dyed black, and has of course been enfeebled by the extra boilings, &c., which it has undergone.

Silk-dyeing.—Silk is usually dyed in skeins, either in the crude state (*souple*) or after it has been ungummed. It is then scoured, bleached, and sulphured; the latter only when the silk is to be dyed with very bright colours and delicate light hues. Silk is chiefly dyed in cold dye solutions. It is dyed black by any of the following processes:—

1. Logwood and iron mordant;
2. Logwood and potassium bichromate;
3. Galls and other substances containing tannic acid with iron salts as mordant;
4. With aniline black, according to the recipes of Persoz, jun., and others, by the use of copper chromate and aniline oxalate.

The first and second are simply known as ordinary blacks, while the third is known as fast black. The ordinary black is obtained by simply mordanting the silk with iron nitrate, and then dyeing it in a decoction of logwood. This cheap dye is more particularly applied to light silken fabrics. The colour is reddened even by weak acids, such as lemon and orange and other fruit juices. The fast black is far more expensive, but it is not affected by weak acids, while it affords the additional advantage of largely increasing the weight of the silk (in the raw state, as well as in spun yarn, silk is sold and bought by weight), as this textile fibre absorbs from 60 to 80, and even 100 per cent. of its own weight, and silk used for shoe-laces even 225 per cent. of the dye material. When desired, the silk-dyer has, for 100 lbs. of raw silk delivered to him, to return from

160 to 180 or 250 lbs. of dyed material, the increase being obtained by "weighting." In England nut-galls imported from the Levant are employed to dye silk black. Although the increase in weight of the silk by black dyeing is advantageous to the dealers, the depositing of so much foreign matter in the fibre of the silk, not only injures its wearing qualities, but also gives rise to the disagreeableness of the dye coming off while the material is being worn. Microscopic research has proved that the dye adheres very loosely to the silk. The process of dyeing silk black with galls is very simple. The fibre is first steeped in a solution, or rather infusio-decoction, of galls, technically known as "galling," after which the silk is placed in a solution of iron nitrate. This black is sometimes dyed on silk previously dyed with Prussian blue, but far more frequently a bluish shade is given to black by first dyeing the silk with logwood, copperas, and some copper sulphate.

As regards the weighting of the silk, it is essentially due to the fact that silk, as an animal product, has the property of combining with tannic acid and thereby becoming heavier. The larger, therefore, the quantity of tannic acid contained in the dye-bath, or the oftener the galling of the silk is repeated, the heavier, within certain limits, will the fibre become. It is not quite indifferent whether a ferric or ferrous salt of iron be employed, the former being preferable. The previously galled silk becomes, when passed through a solution of ferric salt, at once coloured black; but when it is passed through a solution of a ferrous salt, the silk becomes at first coloured only black-violet, and gradually deep black by exposure to air. Although in every case the result is the same, the use of a ferric salt is advantageous, and becomes necessary with a small quantity of tannic acid, while for a heavy weighting of the silk the ferrous salt of iron only can be employed. It is stated that the dyeing of silk with aniline black by means of copper chromate and aniline oxalate yields excellent results.

For some years silks have also been dyed with an aniline black got up with ammonium vanadate.

Blue Dyeing.—Silk is dyed blue either with indigo, Berlin blue, logwood, or aniline blues. The indigo vat has not been much used for imparting a blue colour to silk since the discovery of fixing Prussian blue upon silk; and if indigo is used at all it is as indigo extract, or the so-called distilled blue—purified sulphindigotic acid. In order to dye silk with Prussian blue, it is first immersed in a solution of iron nitrate. This salt is generally in use in England, while in France iron persulphate made by dissolving green copperas in nitric acid is employed, and known under the name of Raymond's solution, the blue produced being termed Raymond's blue; Napoleon blue is produced by the addition of a tin salt to the iron bath, followed by treatment with a solution of potassium ferrocyanide acidulated with sulphuric acid. The latter blue, more brilliant than the former, is usually preferred in England, a tin salt being invariably added to the iron mordant. The mordanted silk is next passed through a boiling soap solution, then washed, and next steeped in a solution of potassium ferro-cyanide acidulated with hydrochloric acid. The brilliancy of the dyed silk is greatly enhanced by passing it through water containing ammonia. Dyeing silk with aniline or naphthaline blue is a very simple process, it being only necessary to put the silk into a solution of the dyes, the solvent being alcohol or wood-spirit, or, in the case of soluble aniline blue, water. The silk is left in the solution until it has assumed the desired hue.

Until very recently silks were dyed red with safflower (carthamine), cochineal, and orchil. Now magenta, coralline, saffranine, eosine, and Magdala red are employed.* Violets are still dyed on silk with orchil, which is being gradually superseded by methyl and benzyl violet.

* None of these tar colours surpass, even if they equal, carthamine in beauty. No true rose can be dyed with magenta. The finest reds on silk are now produced with the eosines.—[EDITOR.]

Yellow Dyes.—Yellow is produced upon silk by first mordanting with alum and dyeing in a decoction of weld, to which, if it be desired to impart an orange hue, some annatto is added, or, preferably, Manchester yellow. By cautious treatment with nitric acid, silk may be dyed yellow, some xanthroproteic acid being formed, while, without any mordant, picric acid produces a bright lemon-yellow on silk, the colour becoming deeper by treatment with alkalies. The production of picric acid upon silk by the action of nitric acid is not now in use.*

Green Dyes.—Silks are now dyed green almost exclusively with methyl green and malachite green.

Cotton-dyeing.—Cotton is dyed either as yarn or woven fabric, but more generally as yarn. Cotton is far more difficult to dye than wool, and requires, especially for obtaining fast colours, stronger mordants. Blue is produced upon cotton (which, when woven, is termed calico) by means of the copperas vat (*see* Indigo); further, by Berlin or Prussian blue, logwood, and green copperas; and, finally, by being passed through a solution of copper oxide in ammonia, the fibre, yarn, or tissue after drying exhibiting a beautiful bright blue colour. Yellow is produced with Persian berries, weld, fustic, quercitron, annatto, iron acetate, technically known as black liquor (nankeen), and chrome-yellow. Green is obtained by the copperas vat followed by dyeing with fustic. Brown is produced with a salt of iron and with quercitron or madder, or simply by means of hydrated manganese oxide. Black is either a fast aniline black, or is produced by dyeing blue by the aid of the copperas vat, next mordanting with iron acetate, and then dyeing in a bath consisting of galls and logwood. The majority of the aniline colours can be fixed upon cotton only by the aid of a specific mordant—a solution of tannin in alcohol; or the fibre of cotton is first *animalised*, as it is termed—that is to say, impregnated with either albumen or casein, the fibre being thus to a certain extent made similar to that of wool or silk, and rendered absorbent of aniline dyes. Cotton may be mordanted with Gallipoli oil or for certain dyes with soft soap.

A very important observation has been made by Witz, Cross, and Schmidt, that cotton oxidised by chloride of lime, chloric acid, &c., readily takes up colouring-matters. The bath employed is a solution of potassium chlorate, saturated at common temperatures, and containing to 1 mol. $KClO_3$ less than 1 mol. HCl, but more than $\frac{1}{5}$ mol. and 0·01 gramme vanadium per litre in the state of chloride. The cotton, whether loose, as yarn or as cloth, and whether crude or scoured, is steeped in the solution and then wrung out, or, after insertion in the liquid, it is quickly exposed to a heat of 60°, until the formation of chlorous acid is indicated by vapours or by the appearance of a yellow colour. Or there is used as an oxidising bath a solution of potassium dichromate, saturated at common temperatures, and acidulated with 1 to 2 mols. hydrochloric acid or sulphuric acid to 1 mol. $K_2Cr_2O_7$. The cotton is steeped in this liquid for thirty minutes. If it is desired to increase the action, the liquid may be slightly heated, or the effect may be reduced by the addition of water. In every case the cotton is thoroughly washed after oxidation, and it is then ready for dyeing.

According to a process given by the Baden Aniline Company, cotton (loose, in yarn, or cloth) is placed in a bath of from 30 to 40 grammes turkey-red oil (sulphoricinate) per litre, whizzed, and dried at from 50° to 60°. As a chrome mordant there is used a basic chromium chloride, obtained by dissolving precipitated chromium hydrate in an insufficient quantity of hydrochloric acid. The oiled cotton is soaked in such chromium chloride at 14° Tw. for from two to three hours, turned out, and washed. To remove all mineral acids, it is taken through sodium acetate at 5 grammes per litre and washed again. The goods are then ready to be dyed. Calcareous water must be neutralised or

* Picric acid cannot be used for dyeing handkerchiefs or other articles which have to be washed, as the colour is discharged.—[EDITOR.]

acidified to prevent the formation of an insoluble lime-lake of alizarine blue or ceruleine. Light shades require 3 per cent. of alizarine blue (S) or ceruleine, and dark shades require 6 per cent. The flot is heated slowly and gradually; cotton-wool is kept in it for two hours at from 70° or 80°, whilst yarn and cloth are boiled for an hour. After dyeing, the steaming follows, at once in the case of loose cotton, but after a repeated oiling in the case of yarn or cloth. The process is concluded by washing and soaping. Alizarine red and orange can be dyed under the same conditions in the chrome bath.

C. Koechlin mordants the cotton in a bath containing to 100 kilos. of goods 10 to 12 kilos. of tin crystals, 5·3 kilos. of stannic chloride at 115° Tw. (= 3 litres), and 2½ kilos. sulphuric acid at 154° Tw., together with water enough to wet the cotton thoroughly. The hanks, after being wrung out, are left lying over-night, washed well, and then taken through a bath of from 40 to 50 grammes of soda-crystals per litre at 40°. The cotton, when washed, is ready for chroming. It is worked for an hour at 80° in a beck of from 40 to 50 grammes chrome alum per litre. Probably the use of basic chrome salts, as $Cr_4(SO_4)_3(OH)_6$, would be better. H. Koechlin uses chromium acetate.

The solid violet obtained by H. Koechlin by the action of nitrosodimethylaniline upon gallic acid, after it has been rendered soluble with sodium bisulphate, can be at at once dyed upon cotton mordanted with chrome, and yields fine violet-blue tones, which approach aniline violet in brightness, but are distinguished by their far greater fastness. If solid violet is dyed along with yellows, such as bark or berries, &c., we obtain deep blues, resembling indigo. According to the tone desired, the bath is made up with from 10 to 15 per cent. of solid violet (calculated on the weight of the cotton) and from 6 to 12 per cent. extract of bark at 14° Tw., with the addition of from 1 to 2 per cent. tannin and from 0·1 to 0·2 per cent. methylene blue. Piece goods may be dyed in this flot in a jigger. They are entered at the common temperature, which is then gradually and regularly raised in an hour and a half to 70°, at which temperature it is allowed to remain from a quarter to half an hour. The bath is completely exhausted, and the pieces are then washed and dried. If they are steamed, the colour not merely becomes much deeper, but also much faster. The colour also yields better if the alkaline chrome bath is applied to pieces which have been prepared in a bath of tin chloride (1 litre $SnCl_4$ at 114° to 16 litres water). The blue thus obtained bears soaping, exposure to light and dilute acids, and, if it is not as fast as vat blue against alkaline carbonates, it has the advantage of not smearing off. The fibre is dyed through and through, whilst indigo is deposited more on the surface, and therefore rubs off on repeated washing and the accompanying friction. A further advantage of the fast blues obtained with solid violet is the ease with which their tone can be modified at pleasure from the purest violet to the greenest blue by merely changing the proportions of violet and bark-liquor, whilst indigo does not admit of such modulations.

Turkey Red.—Of the three similar processes, that with turkey-red oil is the most important. The bleached and dyed cotton is saturated by steeping or padding with a solution of from 10 to 15 kilos. of saturated turkey-red oil (50 per cent.) to 100 litres water. The excess is drained off and the cotton is dried. It is steamed for from sixty to ninety minutes, and then worked for from two to four hours at a hand-heat in red liquor or in a solution of basic aluminium sulphate, $Al_2(SO_4)_2(OH)_2$, at 7° Tw.

After mordanting, the excess of the aluminium salt is removed in a centrifugal, and the cotton is dried and washed in cold water, or first treated for half an hour at from 40° to 50° in a chalk bath containing from 20 to 30 grammes ground chalk per litre. Alkaline fixing agents, such as ammonia and sodium carbonate, must be avoided, as they would strip off a part of the oil preparation. Then follows dyeing, with from 15 to 20 per cent. of alizarine (10 per cent. strength), with the addition of 1 per cent. of its weight of chalk or calcium acetate. The cotton is dyed in the cold for half an hour to secure a level colour, and the temperature is then gradually raised in the course of an hour to 70°,

and the dyeing is continued at this temperature till the bath is exhausted. The cotton is next thoroughly washed, avoiding very calcareous water, the excess of liquid is removed with the centrifugal, and the cotton pressed and dried.

The dyed and dried cotton is again saturated with a dilute solution of neutralised turkey-red oil (from 50 to 60 grammes to the litre), and dried. This second preparation may also take place after the mordanting, in which case the oil is fixed upon the fibre by a second treatment with a weak solution of basic aluminium sulphate. The dried cotton is again steamed for an hour as before, and raised with soap and stannous chloride.

Aniline-black Dyeing.—In the old process, chiefly used in printing, the black is developed in the so-called oxidation-rooms, *i.e.*, chambers in which the goods printed with the black colour, after being quickly dried in a drying chest, are hung up to oxidise. This hanging process is suitable only for the development of patterns, but not for giving calicoes a uniform black ground, since, wherever the tissue is not exposed to the air in a uniform tension, lighter stripes remain, which cannot be removed by any subsequent treatment. Wherever a black ground is required, it has been found advisable to develop the black in a steam chest, in which the mordanted pieces are oxidised merely by steaming, without the intervention of drying. This steam aniline black, however, does not equal the blacks produced by oxidation in the air in respect to beauty and purity of colour.

The third process, now very generally used for cotton yarns, both in hanks and in warps, depends on the use of a metallic salt, generally potassium chromate, to effect the oxidation in the formation of aniline black. But this process is not suitable for producing blacks on piece goods, for not only is it very difficult to obtain a uniform dye in this manner, but this aniline black smears off, as it is not perfectly attached to the fibre. Hence it follows that the black produced by oxidation, as it does not smear off at all, surpasses every other aniline black in quality.

As far as piece-dyeing is concerned, the original process has been very widely resumed, but the drying and oxidation processes take place in a long chest in which the tissue, saturated with the mordant, is passed slowly up and down, stretched out equally. The interior of the apparatus is kept at a temperature of from 44° to 50° by means of hot-air pipes, and the vapours and gases given off are drawn away uniformly the entire length of the chest. The drying and oxidation of the mordant take place in the front of the chest, and fresh air of about 25° streams constantly from below into this part of the chest and between the tissues. As soon as the goods thus dried and oxidised arrive at the back part of the apparatus, which is completely closed, they begin to show colour. At the end of the chest there are placed between the folds of the tissues, some water-troughs, to ensure a moist atmosphere, which is essential for the production of a good black.

Linens are dyed like cottons, but the process is more difficult, as the affinity of the linen fibre for colouring-matters is still feebler than that of the cotton fibre.

Tissue-printing.—The most important part of tissue-printing is cotton- or calico-printing. It depends on the same principles as dyeing, but it has much greater difficulties to encounter, partly because only certain given spots have to take up the colours with well-defined outlines, whilst other parts remain colourless or have to be deprived of colour, and partly, again, because several colours have to be produced in juxtaposition. There is further required a pleasing, tasteful, and artistic arrangement of the colours. The colours applied in tissue-printing may be divided into two main classes—those in which the colours are at once placed directly upon the cloth by means of engraved rollers or plates (application colours), and those which are obtained by the immersion of the tissue in a dye bath (generally called pan or madder colours). To the former belong the iron colours, Prussian blue, madder lake, indigo, cochineal, and most of the coal-tar colours. In the second class fall madder and alizarine, cochineal, logwood,

weld, sumac, &c. If steam is used to fix the colours upon the tissue, we have the steam styles. If the colours are of an inorganic nature (ultramarine) or lakes (madder lake), which are fixed mechanically—*i.e.*, by the help of albumen, caseine, gluten, or oil varnish—we have the pigment style. The pan colours are more generally applied in calico-printing. The tissue is passed into the dye pan as if it was to be dyed of one colour, but by various means the colour is only attached locally.

If the colouring-matter requires a mordant for its fixation, this is often printed on alone, and, after dyeing, there is thus obtained a coloured design upon a white ground. If, *e.g.*, the cloth is printed with thickened red liquor and dyed up in the madder (alizarine) beck, the mordanted parts only are dyed red, &c. In this manner are obtained the so-called madder styles. Or the parts which are to remain white are printed with a *resist*, *i.e.*, a preparation which hinders the colouring-matter from attaching itself to such parts. Thus in the case of indigo we use as resists copper acetate or sulphate; if cloth thus printed is passed into the indigo vat, the ground is dyed blue whilst the design remains white.

There is often added to a resist a mordant for some other colour, so that the places which remain white in the vat may take up some other colour in a dye beck, which acts merely on the resisted or the reserved parts. Here belongs the so-called lapis style.

The cloth may also be uniformly mordanted or dyed, and then the mordant or the colour is removed in parts. The agents employed are called discharges (Fr. *enlévages*, Ger. *Aetzbeizen*). If the cloth is first uniformly treated with a mordant and then printed with a discharge (*e.g.*, citric or tartaric acid), which dissolves the alumina or the iron oxide of the mordant, then on dyeing we obtain a white design on a coloured ground. A similar result is obtained by printing a suitable discharge on dyed cloth. Such are either oxidising agents (like chloride of lime and chromic acid) or reducing agents (like salt of tin or ferrous sulphate).

Here may be mentioned a curious application of photography to tissue-printing. The cloth to be printed is padded with a preparation sensitive to light, then covered with a thick black paper in which the pattern is cut out, and exposed to the sun, when the parts not protected are coloured. The matter susceptible to light is then removed.

The above-mentioned processes can be almost indefinitely modified for the production of certain designs. Thus, if a cloth has been printed with mordants and dyed, the mordanted parts appear coloured upon a white ground. Upon this ground other mordants or colours may be blocked in. Colours which have been already produced may be modified by printing upon them other mordants or colouring-matters, thus producing conversion colours (*couleurs de convertion*).

The pieces which are to be printed are singed, bleached, and calendered by a passage between rollers to press the threads of the tissue smooth, so as to give the cloth a perfectly even surface to which the mordants and colours may be applied uniformly. The cloth is then printed.

*Thickenings.**—In order to give the colours or mordants used in printing, either by block or cylinder, a sufficient consistency, they are mixed with what are technically known as thickenings. As such are used—Gums senegal and tragacanth, leiocome, British gum, dextrine, salep, flour, gluten, pipe-clay with gum, glue, and size, lead sulphate, sugar, molasses, glycerine, starch, sometimes zinc chloride and nitrate.

* If the intensity of the colour produced by means of a mordant is inversely as the quantity of the solids which the mordant requires for the thickening, the reason lies in the property of solids to form with a portion of the mordant, a compound upon which the tissue has no action, and, partly, also because a colour which contains less solid matter in a given volume, when dyeing, undergoes a kind of fading which is far greater than when the thickening predominates.—[EDITOR.]

The purity of the colours and the distinctness of the outlines depend on the right selection of the thickeners. Not every substance which has the property of rendering liquids glutinous can be thus used. Thus, sugar is generally excluded in consequence of its tendency to deprive the mordants of their affinity for the fibre. In the selection of a thickener for any particular case the colour-mixer has to be guided by the following considerations:—

1. He must attend to the temperature necessary for thickening a colour; if, *e.g.*, a colour is apt to be decomposed in heat, flour and starch are not admissible, since these substances thicken only when mixed hot.

2. The reaction of the colour or mordant is important. If it is very acid, flour, starch, and dextrine are excluded, since these substances are liquefied by the action of the acids, and form products which have often an injurious action upon the colours. If the reaction is alkaline, the question is does it contain earths or metallic oxides: in the former case all thickeners which are coagulated by alkalies, such as flour and starch, are excluded, but gums and dextrine are admissible; in the second case no thickener which forms insoluble compounds with metallic oxides must be admitted.

3. All decompositions between constituents of the colour or the mordant and those of the thickener must be avoided; thus, basic lead acetate precipitates most of the thickeners above mentioned with the exception of sugar. Ferric salts are coagulated by gums tragacanth and senegal, and must therefore be thickened with starch or dextrine. Stannic chloride and iron tannate are not coagulated by gum senegal, but by all other thickeners.

4. The consistency of the colour is to be regarded, as the speed with which it dries may have a great influence upon the intensity of the colour as it appears on the calico. Thus, iron and aluminium mordants (which are distinguished for drying rapidly) do not give such full colours if thickened with gum as if starch had been used.

5. The intensity of the colour to be produced is often important. A mordant thickened with tragacanth or starch paste yields stronger tones than if gum senegal or dextrine had been used.

6. The colour of the thickener is unimportant only if the colour printed upon the tissue can bear cleansing and the removal of the thickener without injury. If, in printing woollens with rose or blue, two colours which do not bear washing well, they are thickened with dextrine, the former would take a brownish and the latter a greenish tone. Upon calico, on the contrary, both colours can be safely thickened with dextrine, as in this case a thorough washing is practicable.

7. The ease with which a thickener can be removed from the cloth is often decisive. Even a colourless thickener may, in proportion as more or less of it is left upon the tissue, have an injurious effect upon the colour, and give the cloth properties which impair its value.

8. The degree of contraction to which the tissue is exposed by some thickeners is important, especially if several colours have to be printed on in succession. If a very thick solution of gum is printed upon cloth, it contracts in drying and causes the cloth to shrink unequally, producing unevennesses, which render the subsequent accurate application of other colours impossible. To avoid this evil there is used a mixture of thickeners, which counteract, or at least reduce, this shrinkage. Thus, the solution of gum is sometimes mixed up with pipe-clay, lead sulphate, or glycerine, which effects a mechanical division of the gummy mass.

9. The succession in which the colours are applied after each other, or upon each other, is important, for, if we merely regard the mordant, the design may easily suffer by the mutual action of the thickeners upon each other and by their colours. The

colour to be printed on first is generally the darkest, and is thickened with starch, whilst the next is thickened with gum. In fine cylinder work with three colours, the first is thickened with dextrine, the second with starch, and the third with gum senegal.

10. The manner of producing a design is also important. If it is very delicate, starch and flour are inadmissible. Thin colours must be used for shallow engraving.

Madder Style.—Calico-printing in the dye beck (otherwise called dyeing upon mordants) is effected by printing the cloth with mordants, and, after fixing and drying them, dyeing up with madder, alizarine, or other colouring-matters, when only the mordanted parts become dyed, whilst the ground remains white, or takes up merely so little colour that it may be completely removed by a soap or a bran bath, or by a slight chlorising.

Madder printing is effected as follows:—

(*a*) The mordant is printed on with the cylinder machine. If flowers have to be produced in which red, brown, and black occur, the mordants are put on simultaneously with three cylinders—with the one, red liquor thickened with flour or starch; with the second, a mixture of red liquor and black liquor; and with the third, black liquor (an iron mordant). The following may serve as specimens of the composition of the mordants:—For red liquor, 188 litres water, 50 kilos. alum, 5 kilos. soda, and 38 kilos. sugar of lead; the mordant decanted off from the lead sulphate marks 16° to 16·5° Tw. To "sighten" the mordant—*i.e.*, to show where it has been applied—1 litre of this liquid let down to 6·75° Tw., 120 grammes starch, and a little red-wood or logwood liquor are taken. According to another formula, we take, to 100 litres water, 35½ kilos. alum, 24½ kilos. sugar of lead, 4 kilos. soda crystals, and 2 kilos. common salt. The liquid decanted off from the sediment is mixed with 45 litres zinc nitrate at 1·11 sp. gr., thickened by boiling with 2½ kilos. starch, and sightened with 100 grammes neutral extract indigo dissolved in vinegar. For the black mordant, take, to 1 litre ferrous chloride at 9° Tw., 130 grammes starch and 130 grammes wheat flour. The colour, mixed by boiling and stirring, is intimately incorporated with 15 grammes olive oil.

Printing on the mordants is not always merely the first step. Frequently, if it is intended to produce a full and a light red along with brown and black, red liquor of the proper concentration is first printed on by two cylinders, then air-dried, dunged, and dyed up in the madder beck. The black liquor and the mixture of red and black liquors for browns are blocked in by hand, aired, dunged, and dyed up in a beck of madder and sumach.

(*b*) *Drying and Ageing.*—If the cloth were dried in the air just as printed, the mordant would in many cases spread and spoil the outlines of the pattern. Hence it is important that the pieces, when dry, should hang for at least thirty-six hours in a heated chamber, that the mordants may be fixed insolubly upon the fibre.

(*c*) The dunging process serves not merely to effect a more intimate combination of the base of the mordants with the fibre, but to remove a part of the thickening and the sightening colour, as well as any uncombined parts of the mordant.

(*d*) The dyeing in the madder or the alizarine beck is effected either in a single process or in two operations. For dyeing in a single operation the beck is filled with water. As soon as the temperature has reached 35°–45°, the madder is introduced, and the pieces are run over the reel in the beck, which is kept in constant motion during the dyeing. The temperature of the beck is slowly raised so as to reach 50° in half an hour, and after another hour 70°, at which the beck is kept for another half an hour, and is then gradually raised to a boil. When the dyeing is completed the pieces are wound off the reel, and washed. Light shades are generally dyed only once; for full shades, especially for red grounds, the dyeing is performed twice. For the success of the

process, it is necessary that the mordants should be thoroughly saturated with colouring-matter. This is especially the case for colours which have to be raised or taken through flots of other colouring-matters. If, *e.g.*, it were intended to print upon the white ground of the cloth, after maddering, red or black liquors, and then dye them up in the quercitron bark beck, the first mordants, if not fully saturated with the madder colour, would take up a yellow colouring-matter, and thus convert the red into an orange and the violet into a grey olive-green.* That a mordant is not saturated with colouring-matter is known because during dyeing the flot becomes clear and exhausted, and the different tones are not sharply distinguished. Until they have taken up their maximum of colour they seem almost alike. The want of colouring matter is detected too late when the dyed pieces lose their colour in bleaching. A certain sign of unsaturated mordants is a change of colour when the goods are passed into a bark beck.

Among the ordinary colouring-matters fixed by means of alum and iron mordants, that of madder has the greatest affinity for the bases, and cannot be eliminated by any other colouring-matter. Hence every change of colour in a beck other than one of madder is a certain sign of incomplete saturation.

In dyeing mixed colours with madder and other dye-wares whose affinity for the mordants is not equal, care must be taken that no more madder is used than is exactly needed, unless the dyeing is effected in two separate operations.

Witz utilises oxycellulose for calico-printing by means of the chlorates. Chloric acid can be substituted for the hypochlorites if it is brought into contact with the fibre under such circumstances that it is resolved into oxygen and unstable oxides of chlorine under the influence of the reagents which it meets. Vanadium salts decompose chloric acid most easily and rapidly. A saturated solution of potassium chlorate mixed with rather less hydrochloric acid than the quantity required to set free the chloric acid, thickened with gum tragacanth and with 10 milligrammes vanadium per litre, is printed on the cloth. On drying at a temperature of from 50° to 60°, the formation of oxycellulose takes place. The quantity of chlorate and of vanadium may be reduced according to the temperature and the duration of the reaction. Steaming is less advantageous than hot air. Quick, sharp drying evolves a strong odour of chlorine, and leads to energetic oxidation, which, however, is not attended with any notable injury to the fibre. For printing, composition "doctors" are preferable to those of steel. Though the chief action of the chloric acid takes place during drying in the hot air, yet, in order to prevent injury from the acid vapours, the pieces must hang for some hours in a warm room, which must be well ventilated. Or the cloth is padded with a 10 per cent. solution of potassium bichromate, and dried. A starch paste containing 15 per cent. of oxalic acid is then printed on at a hand-heat. The goods are dried, washed, taken through weak sours, and washed again. On dyeing in a cold beck of methylene blue, the design comes up in ten minutes as a deep blue on a pale blue field.

By "padding on mordants" is understood a process by means of which the cloth is saturated with a mordant over its entire breadth, in order either to apply different colours to it topically, or to dye it entirely, forming a coloured ground upon which coloured designs may be produced by printing on mordants and dyeing them on white designs by printing on discharges.

The machine used in this operation consists essentially of two brass cylinders wrapped round with thick layers of a cotton tissue, and a colour trough placed beneath. The piece to be padded passes first into the trough, where it is saturated with the mordant, and then between the rollers, which are pressed together by a weighted

* English calico-printers unfortunately speak of madder violet as "purple," which leads to some confusion.—[EDITOR.]

lever, which promotes the absorption of the mordant into the cloth, and at the same time removes the superfluous liquid. The pieces are generally passed twice through, the pressure being stronger the second time. Red liquor, black liquor, and mixtures of both can be applied by means of the machine with great uniformity. In order that in drying the padded pieces there may not take place any accumulation of the mordant, which would occasion spots in dyeing, the pieces are either stretched out horizontally or they are passed on guide-rollers through drying-stoves. The dried goods are washed, dunged, printed with the colour, washed, and raised if necessary. This process is especially suitable for inorganic colours in buff, Prussian blue, manganese or bistre brown, chrome yellow, and chrome green.

Printing with Resists.—Sometimes there are applied to the cloth, at places which are to remain white, certain substances which prevent dyeing. Such substances are known as resists. In most cases a resist serves to prevent the absorption of indigo in the vat at the reserved places. In tissue-printing there are four different kinds of resists—the fatty, the white, the coloured, and the so-called lapis.

Fatty Resists are used chiefly in silk-printing, sometimes in woollen-printing, but rarely on calico. They consist generally of wax or ceresine, or a mixture of resin and tallow, or resin and paraffine, sometimes of an emulsion of tallow, palm oil, and gum mucilage. Now and then fatty resists are used on cottons. If, *e.g.*, a red or violet pattern has been printed upon a white ground, dyed, and raised, and it is intended to produce also a lighter purple colour on the ground, the pattern is provided with a fatty resist, and the pieces are taken through a dilute iron mordant, proceeding exactly as in the madder style. As the designs are covered, the colours reappear, after the second raising, with their original shade.

White Resists.—A very common constituent of white reserves is a copper salt, blue-stone, or verdigris, which is thickened with pipe-clay and gum. On dyeing up in the vat, its alkali decomposes the salt of copper, forming at once insoluble indigo-blue from the dissolved indigo-white.

Coloured Resists not merely prevent the indigo-blue from being deposited on the reserved parts, but also produce other colours in these reserved places. In this manner buff and chrome-yellow designs can be obtained on a blue ground.

Lapis Style.—This manner of printing consists in a combination of the madder style and of indigo-vat colours. The mordants intended for the madder colours are mixed with the resists, printed, dyed in the vat to the shade intended, and then dyed in the madder or in the bark beck, and the whites are cleared. The lapis style yields not only very fast, but very manifold, products, in consequence of the numerous modifications which it admits of, and it is hence extensively used. It derives its name from a certain resemblance of the patterns thus obtained upon a blue ground to *lapis lazuli*. The white resists in this style have not merely to protect certain parts from the action of the vat, but to keep them unmordanted, so as to consume as little colour as possible in the madder beck. In this case mercuric chloride is preferred to copper sulphate.

Two kinds of white resists are used in the lapis style. The one kind acts like the ordinary resist containing copper oxide—*i.e.*, it covers, without exerting any action upon, the mordants beneath, so that it may be safely printed over mordants for dark or light reds without interfering with their subsequent action. The other kind renders the mordant ineffective. To this latter kind belongs a resist made up of 1½ kilo. sodium arseniate, 1½ kilo. gum senegal, 2 kilos. pipe-clay, and 4 litres water, with which are incorporated by boiling 500 grammes olive oil and 375 grammes mercuric chloride. The arsenic acid forms, with the ferric oxide and the alumina of the mordants afterwards printed on, insoluble arseniates which have no affinity for the fibre. A resist of the first kind is composed of a mixture of 0·5 kilo. gum senegal, 1 kilo.

pipe-clay, 180 grammes olive oil, and 2 litres water, to which 180 grammes mercuric chloride are added.

Discharges are to effect the local removal of the mordant printed upon the cloth by means of thickened acids. On dyeing there is obtained a white design on a coloured ground. Or an acid, by itself, or mixed with a mordant, is printed upon the cloth, upon which a dark mordant is then padded and the piece is dyed. The parts printed with the acid remain white, forming white designs on a coloured ground.

The acids used as discharges act upon the metallic oxides in the mordants and form with them soluble salts, liberating the fibre from the mordant. The common mineral acids (sulphuric, nitric, and hydrochloric) are otherwise suitable for this purpose, but they are apt to weaken the fibre, whence organic acids (such as malic, citric, and tartaric) are preferred, as they do not tender the fibre and have little action upon the doctors and the rollers. Phosphoric and arsenic acid at sp. gr. 1·85 may be used instead of tartaric acid, as can also hydrofluosilicic acid. Instead of 1 kilo. tartaric acid there may be used from 1·25 to 1·5 kilo. of liquid phosphoric or arsenic acid. The latter has the grave defect that it attacks the hands of the workmen, destroys the finger nails, and is highly poisonous. Oxalic acid is commonly used in the proportion of from 12 to 15 per cent. to tartaric acid. It has the property—very important for the preparation of steam colours—of dissolving alumina and ferric oxide in the cold and of re-depositing them at higher temperatures in an insoluble condition.

Stannic chloride may also be used in place of tartaric acid: 11 parts of the commercial salt, as free as possible from acid, serve instead of 10 parts of tartaric acid. Stannic chloride (with which lime is mixed, the quantity depending on the proportion of acid) acts by liberating chlorine, forming calcium chloride, and separating tin hydroxide. If an iron mordant has to be removed, stannous chloride is to be used, which dissolves the iron mordants in virtue of its reducing power, whilst stannous oxide is converted into stannic oxide, which partly remains on the fibre. Hence, in using tin salts as a discharge, it must be remembered that a tin mordant takes the place of an iron mordant, and the colour produced in the dye beck will be modified accordingly.

Discharges are thickened with gum senegal and pipe-clay in order to obtain well-defined outlines; for heavy designs, dextrine may be used.

Discharges are often combined with ordinary mordants. Thus, if it is intended to produce a red-and-white design upon a purple ground, the calico is padded with weak black liquor, and, when dry, red mordant mixed with citric acid is printed on. The iron mordant is thus removed at these places, and an aluminium mordant is substituted. A discharge is printed at the places which are to remain white, and the cloth is cleansed with milk of lime, dunged, dyed in the madder beck, and raised.

China-blue Style.—This style (otherwise known as Fayence blue) was often used for producing blue designs on a white ground. The process is very old, and has been used in India for centuries. It is a topical style, which can be effected only with indigo. Its peculiarity is that the indigo is applied in the insoluble state, dissolved, and then fixed on the fibre.

A very intimate mixture of finely ground indigo and copperas is printed upon a white ground, and it is then dissolved and reduced by alternate treatment with lime-water and solution of copperas. The indigo penetrates, as indigo-white lime, into the fibre, and in contact with the air the indigo-white is oxidised to indigo-blue, rendered insoluble, and thus fixed upon the fibre. To improve the action, orpiment is commonly added, which acts similarly to copperas and prevents higher oxidation.

Pencil blue is distinguished from china blue as follows :—In the latter, indigo-blue is printed upon the fibre, and is then converted into indigo-white, whilst in pencil blues an indigo-white, already prepared, is printed upon it. To obtain more concentrated solu-

tions, orpiment is used, which reduces indigo-blue just as copperas does. The arsenical or orpiment vat gives a very intense colour, which is thickened with gum, and applied to the tissue by means of small pencils, whence the name pencil blue. Instead of the or orpiment vat the tin-crystal vat may be used for the production of a pencil blue.

The discharge style aims at the local removal of a colour already printed on by means of oxidising agents, whilst the discharge mordants act, not upon the colouring matter, but upon the mordant; either removing it, or cancelling its character as a mordant.

As a discharge for indigo there is used chromic acid or ferric chloride, or a mixture of potassium ferricyanide with soda; for madder, chlorine is used.

To produce a white design on a blue ground, according to Koechlin's process, potassium chromate is used, which, when decomposed by oxalic or tartaric acid, decolorises the indigo-blue by supplying oxygen, and converts it into soluble isatine, whilst the chromic acid is reduced to chromium sesquioxide. Instead of chromic acid, Mercer proposes to destroy the indigo with a mixture of potassium ferricyanide with concentrated caustic soda (Mercer's liquid). To this end the cloth dyed blue in the vat is saturated with a solution of ferricyanide, and caustic soda thickened with starch gum is printed on. The alkali converts the ferricyanide into ferrocyanide, and the indigo-blue is transformed into isatine by the oxygen liberated.

In order to obtain a white design upon a turkey-red ground, the property of chloride of lime is utilised, not to destroy the colouring-matters by itself, but to act only in proportion as chlorine is evolved by the action of acids. For this purpose the parts to be discharged are printed with an acid mordant and taken through chloride of lime.

The discharges are put together in such a manner as to constitute the mordant for subsequently dyeing the discharged spots; they may also contain colours to dye the decolorised parts. For white there is printed on an acid mixture of tartaric and oxalic acid and lime-juice thickened with gum and pipe-clay; for yellow, a similar mixture containing lead nitrate and sightened with a little potassium chromate. The calico printed with the discharge passes into the chloride of lime liquor, contained in a wooden cistern lined with sheet-lead. On leaving this cistern the cloth passes between a pair of rollers, when it is suspended in flowing water, rinsed, and dried. If the discharge contain lead nitrate to produce white on a red ground, the pieces are reeled through a solution of potassium chromate, and, after rinsing, they are raised by a passage in dilute hydrochloric acid.

According to Steinbach, the solution of chloride of lime is printed on with the cylinder and the cloth is dried on steam drums, when the chloride of lime is converted into calcium chloride and chlorate, the latter giving off oxygen at elevated temperatures and destroying the alizarine. This process has the defect that the reds and the roses are turned distinctly brown.

For printing aniline blacks on dyed cottons the aniline-black colour is made up with 1½ kilo. potassium chlorate dissolved in 40 litres of water; then there are added 4 litres solution of potassium ferrocyanide (28 : 100) and 2·6 kilos. aniline hydrochlorate previously mixed with the quantity of aniline oil needed for complete neutralisation. The bleached goods are taken through this liquid, dried, oxidised in the steaming-machine so that they issue dark green; then they are taken through a chrome bath at 80° (1 litre water to 10 grammes potassium dichromate, 5 grammes soda, and 5 grammes sodium chloride), washed, and printed on as a discharge. For whites: 10 kilos. calcined starch with 6 litres water and 16 kilos. calcium acetate (24° Tw.), boiled; then there are added 5 kilos. sodium acetate and 5 kilos. sodium-lye at 30° Tw. For yellows: 10 kilos. chrome yellow (paste), 6 kilos. albumen water, 2 kilos. sodium acetate, 0·3 kilo. soda-lye at 30° Tw. For reds: 16 kilos. cinnabar, 2 kilos. glycerine, 2 kilos. water, 2 kilos. sodium acetate, 8 kilos. albumen water.

Steam Colours.—For a long time there were known only two methods of fixing colouring-matter on the fibre—*i.e.*, either the printing matter was printed on, which, like indigo in the china-blue and pencil-blue styles, had been made soluble and was again separated on the fibre as insoluble indigo-blue; or, recourse was had to discharges, to discharge mordants, to resist, and discharge styles, upon which the various styles are founded which have been described in the previous sections. Not until 1740 was the attempt made to print on the colouring-matters themselves, and to obtain colours which were afterwards known as application colours. They did not, however, bear washing, and had so little fastness that their general introduction was attended with great difficulty. Gradually it has been found practicable to fix them by steaming, and thus create the steam style, which now plays so important a part in tissue-printing.

The colours almost exclusively used as steam colours require the co-operation of a mordant. Some of them are thickened, printed upon the mordanted cloth, and then steamed. In other steam colours the colouring-matters and mordants are printed together, but they are always added to a body which holds the lake in solution or hinders the combination of the colouring-matter and the mordant to a lake until the operation of steaming. To the latter class of bodies belongs stannic chloride, which is resolved by watery vapours into hydrochloric acid (which is either volatilised or neutralised), and into stannic oxide, which is deposited on the fibre. Aluminium chloride acts in the same manner. Acetic acid is also used in the production of steam colours, and in considerable quantity since the introduction of artificial alizarine. Acetic acid is added to the mass in order to keep the colouring-matter in solution until the cloth is steamed. Recently copper chromate is often used, and proves to be an excellent oxidising agent. The steaming is generally effected under tension in the apparatus of Mather & Platt.

Steam blue is obtained by printing a solution of potassium ferrocyanide and tartaric acid with small quantities of sulphuric acid, thickened with starch, drying, airing, and steaming for half an hour; there is formed hydroferrocyanic acid, which is decomposed at high temperatures, yielding Prussian blue, which is deposited upon the cotton fibre.

Steam colours may also be obtained from reduced indigo when the indigo-white is precipitated by hydrochloric acid from the copperas vat and mixed with magnesia or with magnesium sulphate with an addition of alkali. A good blue may be obtained with 5 kilos. precipitated indigo, 5 litres of gum water, and 0·6 kilo. of magnesia.

Steam green is produced by mixing blue with a salt of lead, printing on the mixture, and dyeing up the cloth after washing and steaming in a beck of potassium chromate.

Steam reds are at present obtained with artificial alizarine.

Schlieper and Baum propose a very curious process of indigo printing. The first step is the careful grinding of an indigo mixture of 25 kilos. indigo, 100 litres water, 50 litres soda-lye at 1·35 sp. gr., and 58·33 kilos. of solid caustic soda. The colours consist of—

	Dark Blue.	Medium.	Light.
British gum . . .	3·00 ...	3·00 ...	3·00
Maize starch . . .	1·50 ...	1·50 ...	1·50
Water	3·75 ...	3·75 ...	3·75
Soda-lye (sp. gr. 1·35) .	16·00 ...	28·00 ...	40·00
Indigo mixture . .	30·00 ...	18·00 ...	6·00

Dark blue contains 55·5 grammes indigo per kilo. of colour, medium blue 33·3 grammes, and light blue 11·1 grammes. These colours are printed on the tissue, which has been padded with a solution of 1 kilo. glucose in 4 litres water and then well dried. After printing, the goods are rapidly dried at from 60° to 70° and then taken

through a small steam chest for from fifteen to twenty seconds, so that the indigo is reduced. They are then passed through cold water for two minutes.

Precipitated sulphur is the only good resist under the new steam blue, 150 grammes sulphur to 1 litre of thickening resists even the darkest blue. A yellow resist consists of 220 grammes cadmium chloride, 140 grammes precipitated sulphur, and 1 litre thickening.

A red resist consists of red liquor, salt of tin, calcined starch, and 150 grammes sulphur per litre; buff and similar colours have from 130 to 140 grammes sulphur to 1 litre thickening.

For a light blue, soda-lye of sp. gr. 1·35 thickened with British gum and starch is printed on cloth which has been saturated with glucose, steamed for fifteen seconds, dried, and the indigo colour padded on with the cylinder. The glucose undergoes a decomposition under the action of the caustic soda, so that the colour is only developed up to a light blue. Very fine designs can be produced in indigo-discharge colours on grounds dyed in turkey red or prepared with turkey-red mordant.

For a turkey-red mordant 40 kilos. of dry aluminium hydrate is heated for three hours with 64 litres soda-lye at 60° Tw. It is made up with water to 300 litres, neutralised with 8 litres hydrochloric acid at sp. gr. 1·15, and water added to make up a volume of 620 litres.

A mordant for padding is obtained by diluting 4 litres of the above mixture with 1 litre of water. The cloth padded in this liquid is dried on the drum, when it turns yellow, but on hanging in an oxidation chamber the original colour returns. The pieces are left till the following day, taken through cold water in a cistern fitted with rollers, washed well, and lastly passed through a chalk beck at a hand-heat in order to convert the sodium bi- or tri-aluminate into calcium aluminate. The mordant, now ready for dyeing, bears sulphuric sours at 11·5° Tw. without losing much of its efficacy, and the red thus produced behaves similarly. The production of the indigo-discharge styles is founded upon this property. The tissue thus mordanted, whether dyed or not, is prepared in glucose, and the indigo colour is then printed on. The pieces are then steamed, washed, aged for a few minutes in the air, passed through sulphuric sours at 11·5° Tw. for from ten to twenty seconds, washed, taken through weak soda, and washed again. The discharged turkey-red pieces are soaped at a boil. The alizarine present below the indigo is dissolved, and the blue appears.

In order to obtain white upon turkey red and indigo-blue the dark indigo colour and a strong soda-lye are printed on, proceeding otherwise as indicated above. Or strong soda-lye may be printed on the turkey-red mordant, steamed to destroy the glucose, dried, and the indigo colour printed on. A light blue appears when the indigo is superimposed on the whites.

Goppelsröder proposes to produce patterns in indigo and turkey-red by means of electrolysis.

In order to utilise the mordanting action of metallic sulphides in steam colours, Schmid thickens those metallic salts whose sulphides can be precipitated by means of sodium hyposulphite (thiosulphate) along with the latter salt and the colouring matter, and prints them. On steaming, an insoluble sulphide is precipitated, and along with it the colouring matter. In this manner there may be fixed in one operation the cadmium, lead and copper sulphides, methylene blue, malachite green, dimethylaniline violet, &c. The tones obtained correspond to those of the sulphides and the colouring matters employed. Thus, cadmium sulphide with methylene blue forms a green; with aniline green, a yellowish green; &c. These colours bear soaping fairly well. A bright yellowish steam green is, *e.g.*, obtained with 950 grammes tragacanth mucilage (200 grammes per litre), 200 grammes crystalline cadmium nitrate, 30 grammes crystal

lised sodium thiosulphate, 20 grammes malachite green, 10 grammes acetic acid at 10° Tw., and 150 c.c. water.

Along with the steam styles rank the processes used, both in printing and dyeing, to produce a metallic appearance on tissues. This operation is called *coppering*. The cloth is covered with an exceedingly thin layer of metallic sulphide, when the colour comes up in thin layers, resembling the elytra of certain beetles.

According to Barlow's process, the pieces are steeped in a solution of copper acetate or nitrate, or corresponding salts of lead, or bismuth, pressed, washed, and then steamed for five to thirty minutes, hydrogen sulphide being mixed with the steam. After steaming, the goods are washed and dried.

Topical or application colours include such as are fully formed when printed, and are freed from the thickenings and acid salts by washings, so that the colours appear intimately combined with the fibre. Some such colours (I.) are applied in solution and gradually pass into the insoluble state upon the fibre, and thus become combined with it and rendered able to resist washing. Others (II.)—indeed, the most—are printed in the insoluble state, and are thickened with plastic substances, by means of which they adhere to the fibre. The chief difficulty in producing such colours consists in finding thickeners which give the colours the violet lustre, and which best resist water.

Examples of Class I. ("Spirit Colours").—According to Schmid, we obtain, *e.g.*, a fine soap-fast chrome yellow by printing 250 grammes tragacanth water (200 grammes per litre), 250 grammes lead nitrate, 550 grammes barium chromate, and 50 grammes water, and subsequent steaming. Red and rose are obtained from red wood and a mixture of stannic and stannous oxides. The red wood (generally sapan) is used either as a decoction or as a solution of the solid extract, to which a preparation of tin is added, or a lake is made of the red wood and dissolved in stannous chloride. The oxide of tin, separated from the tin compound, deposits on the fibre and gradually takes up the colouring matter.

Madder lakes are also often used for obtaining such colours.

A topical black is often obtained from a decoction of logwood and galls, thickened, and mixed with an iron mordant.

The second group of these colours (pigment style) includes those which are applied in an insoluble state ground up with albumen or with an oil varnish. Such colouring matters are ultramarine, umber, chrome yellows, Guignet's green, vermilion, shearings from dyed woollen cloth, metallic powders, &c. As examples may be mentioned ultramarine and gold and silver printing.

In the use of ultramarine in printing, the earliest agent—at once for fixing and for thickening—was albumen, often mixed with gum senegal, both from economical reasons and that the mixture may print more easily. Some printers fix ultramarine simply by a passage through boiling water, and thus obtain purer, but less saturated, colours than by steaming. But fixation by steam is necessary if other pigments, such as Schweinfurt green or violet lakes, are to be fixed along with the ultramarine. Chrome orange and chrome green require peculiar care, as all substances must be avoided which tend to convert copper or lead into sulphides. Colours containing oils are to be rejected, as well as acids and acidifiable substances which may decompose the albumen and evolve from it hydrogen sulphide.

For printing with gold and silver, isinglass is dissolved in water and brandy; on the other hand, powdered mastic is dissolved in alcohol, and the two are mixed. Red bole, previously ground up with brandy, is stirred into the mixture, which then serves as a ground for gold. For silver, pipe-clay is used instead of bole, and the mixture is printed in the ordinary manner. Immediately after printing, leaf gold or silver is applied to the printed parts, which are then pressed down with cotton. When dry, the superfluous

metal is removed with a brush. In order to print with a metallic powder, such powder is stirred into the above-mentioned mixture instead of the bole or pipe-clay. Or the requisite parts of the design are moistened with a solution of gold, which is then converted into the reguline state by means of reducing agents.

Printing with Coal-tar Colours.—These colours may be printed and fixed upon cotton tissues in several manners. Either (1) the thickened mordant is printed on, fixed by drying and airing or by steaming, and afterwards dyed in a beck of the colouring matter, when the colour attaches itself only to the mordanted places. If it is desired to keep the ground clean, the mordant is padded on locally. Or (2) the mordant is mixed with the dye, thickened, printed, dried, and steamed. After printing, the pieces are washed and dried.

The substances used as mordants are numerous—albumen (egg or blood), preparations of gluten, caseine dissolved in caustic alkali or in acetic acid, gelatine or tannate of gelatine, tannin, fatty oils and preparations of oils (sulpholeic acid, sulphopalmitic and sulphoglyceric acids), and certain gum-resins, *e.g.*, shellac dissolved in borax.

In aniline printing by means of gluten, the gluten of wheat is left to itself until it becomes slimy. It is then saturated with sodium carbonate and thus rendered insoluble, washed, redissolved in caustic soda at sp. gr. 1·08, and the solution is diluted. When the cloth has been printed or padded with this liquid and dried, it is steamed and rinsed. The solution of the aniline colour is then used as a dye beck through which the pieces are taken. Or the colour is printed upon the cloth prepared as before, which is then steamed again.

According to certain colour manufacturers (not named), levulates of the colouring bases or mixtures of levulic acid with the colouring matters may be used for printing. Such mixtures are obtained by grinding in a wet mill levulic acid with the colouring base (dry, or preferably rather moist) until a complete mixture is obtained. Thus the goods may be printed with the following mixture:—

183 parts printing blue (induline) as a 25 per cent. paste
500 „ levulic acid
40 „ emulsion of oil
630 „ acetic-starch thickening
100 „ tragacanth tannin (50 parts tragacanth mucilage and 50 parts tannin),

developing the colour by steaming the printed cloth.

"Levuline" blue is obtained by adding 1 part moist induline base to 3 parts levulic acid and mixing intimately.

According to Bötsch, the Congo colours are prepared for printing as follows:—

Benzoazurine Steam Blue.

Water	750 parts
Wheat starch	100 „
Benzoazurine G	50 „
Water	250 „

Chrysamine Steam Yellow.

Water	750 parts
Wheat starch	100 „
Chrysamine	50 „
Water	250 „

These colours are printed on prepared cloth, yielding respectively blue or yellow, or by a mixture of the true indigo-blue to olive according to the proportions; a very nice blue may be produced by adding Victoria blue B or Nicholson blue 6B. The goods

are steamed, according to shade, from thirty minutes to an hour. These colours are all fast, especially if chrysamine predominates. They may also be used for wool. The stilbene dyes (Leonhardt & Co.) may be used in the same manner.

In fixing by means of chrome, the following, *e.g.*, colour may be used for blue:—

Indophenol	2000 grammes
Acetic acid (8·25 Tw.)	10 litres
Tin acetate (31° Tw.)	10 „
Gum	8000 grammes

The mixture is boiled and stirred for half an hour. After printing, the goods are aged for twenty-four hours, steamed for two minutes, preferably in Mather & Platt's apparatus, chromed at 50° for two minutes in a beck of 10 grammes potassium dichromate per litre water, lastly washed and soaped. Indophenol is less advantageous than the two following colours.

If gallocyanine (from gallic acid) is used, excellent results are obtained with the following mixture:—

Wheat starch	150 grammes
Gallocyanine paste (commercial)	1 litre
Tragacanth mucilage	0·75 litre
Acetic acid (10° Tw.)	0·25 „
Turkey-red oil	0·25 „

Boil, stir till cold, and add $\frac{1}{8}$ litre chrome acetate at 50° Tw. and 60 grammes potassium ferrocyanide. The colour is printed, steamed, and treated as usual.

For alizarine blue there are used 120 grammes of a solution containing 100 grammes starch per litre of water, 15 to 20 grammes alizarine blue S, and 30 to 40 grammes solution of chromium acetate (14° Tw.). In place of starch, tragacanth or gum may be used as a thickener. The printed pieces may be steamed without pressure for ten to twenty minutes, when the blue is found fully developed and the pieces are washed, soaped, and dried. The steaming may be effected in two or three minutes in the continuous apparatus. If the bisulphite compound of alizarine blue is used, the colour in the beck is completely used up. The colour produced resists light, soap, and chlorine, and is in this respect faster than indigo. Soluble alizarine blue has, in point of fact, superseded both indigo and ultramarine in a variety of applications.

Propiolic acid is now little applied.

Auramine is printed with tannin and tartaric acid upon vegetable fibre; the colour is very fine.

Printing with aniline black has been previously mentioned.

Attempts have been made, especially by T. Holliday & Sons, to produce azo colours directly upon the fibre, and these experiments have been attended with encouraging results.

Finishing.—After printing, the goods are *finished—i.e.*, taken through starch becks to give the cloth more firmness, dried, folded, and pressed. In finishing furniture prints, white wax or paraffine is added to the solution of starch. In order to give printed muslins the admired velvety feel, there is added to the starch, whilst boiling in water, a small quantity of spermaceti, paraffine, or stearic acid.

Linen-printing is confined to the production of vat-blue cloths with light blue or white designs.

In woollen and worsted printing, topical styles are in use, and the colours are fixed by steaming.*

For producing a discharge blue upon azo colours, the woollen tissue is first dyed

* Space does not allow a description of the methods used for printing mixed cotton and woollen goods.

with ponceau or any desired azo colour. A mixture of solid violet, indophenol, and an alkaline reducing agent is then printed and steamed; the azo colour undergoes the characteristic splitting up on reduction, whilst the blue colouring matters, reduced to leuko compounds, penetrate into the fibre, and, on subsequent exposure to the air, reproduce an insoluble fast blue on a red ground. The following is the composition of the colour:—

Indophenol in powder	4 kilos.
Tin pulp	10 litres
Thick dextrine water (2½ kilos. per litre)	14 „
Water	6 „
Soda crystals	4 „
Solid violet, B.S.	10 „
Glycerine	5 „

The mixture is heated to 60° for half an hour until completely reduced, which is shown by the yellowish colour of the mixture. It is then printed, steamed, and fully developed by ageing.

The processes of silk-printing are generally the same as those of cotton-printing, but greater care has to be taken to keep the whites clear. Either topical colours are applied and fixed by steaming, or various mordants are printed and dyed in the beck as in the madder style.

A peculiar style of silk-printing is founded on the property of nitric acid to colour silks and woollens a permanent yellow, to destroy most colours, but to act upon fats and resins only after some time. This kind of printing is called mandarining. In order to effect a yellow discharge on vat-blue grounds, the silks are printed with a resist of resin and fat, steeped for two to three minutes in an acid flot of 1 part water and 2 parts nitric acid at 50°, and placed in running water. After this operation the silk is boiled off in a soap bath mixed with potash. The parts which have not been resisted are of a fine yellow.

Examination of Dyed and Printed Textiles.—In order to test the fastness of the dye, the sample is first rubbed upon white paper, which must not be stained in the slightest. To pure water it must give off no colour. To ascertain the effect of heat, a swatch is laid between white papers and smoothed with a flat iron. To find the action of light, the swatch is covered with a piece of black pasteboard, or of sheet metal in which two round holes have been cut, and thus exposed to the sun or to an electric light.

Colours which appear unchanged after they have been steeped in 10 per cent. solutions of sulphuric acid, caustic soda, and ammonia may be pronounced fast. Fast colours should not be altered by boiling for half an hour in a 1 per cent. solution of soap.

Whether, in the production of printed calicoes, the colour has been generated within the fibre, or whether it has been applied pre-formed and fastened by means of albumen, or whether both these procedures have come into play, can best be determined by means of the microscope.

If the tissue is teased out with a needle so far that the individual fibrillæ are isolated, these latter appear uniformly coloured and translucent if the materials forming the colour have been applied in a dissolved state. In many colouring matters there appears a granular texture, the characteristic form of the fibre is unchanged, and the colouring matter appears everywhere uniformly deposited within it. In the albumen processes the fibre is not dyed, but at numerous points there appear single coloured rays of coagulated albumen adhering externally. Here and there such may be seen detached from the fibre in consequence of the maceration.

Lenz, Martin, Hummel, and Lepetit have given instructions for detecting the colouring matters on the fibre. (See page 854, *et. seq.*) The following reagents are

employed :—Sulphuric acid 154° Tw., hydrochloric acid 32° Tw., soda-lye at 10 per cent., the strongest ammonia, and equal parts of concentrated hydrochloric acid and stannous chloride (pp. 854–861).

For further information on the tinctorial industries, the reader is referred to :—

A Practical Handbook of Dyeing and Calico-printing. By William Crookes, F.R.S. London : Longmans, Green & Co.—*Dyeing and Calico-printing.* By the late Dr. F. Crace-Calvert, F.R.S. Edited by Dr. J. Stenhouse, F.R.S., and C. E. Groves, F.C.S. (London and Berlin.) Manchester : Palmer & Howe.—*Dyeing and Tissue-printing.* By W. Crookes, F.R.S. London : G. Bell & Sons.—*The Dyeing of Textile Fabrics.* By J. J. Hummel, F.C.S. London : Cassell & Co. (Limited.)—*Dyeing : comprising the Dyeing and Bleaching of Wool, Silk, Cotton, &c.* By Antonio Sansone. London : Hamilton, Adams & Co. ; Manchester : A. Heywood & Son.—*The Printing of Cotton Fabrics.* By Antonio Sansone. London : Hamilton, Adams & Co. ; Manchester : A. Heywood & Son.—*Chemistry of the Coal-tar Colours.* By Dr. R. Benedikt and Dr. E. Knecht. London : G. Bell & Sons.—*Anthracene : its Constitution, Properties, Manufacture, and Derivatives, with their Applications in Dyeing and Printing.* By G. Auerbach. Edited by W. Crookes, F.R.S., &c. London : Longmans, Green & Co.—*Manual of Colours and Dyewares.* By J. W. Slater. London : Crosby Lockwood, & Co.—*Dictionary of Calico-printing and Dyeing.* By C. O'Neill. London : Simpkin, Marshall & Co.

PAPER MANUFACTURE.

History of Paper.—Paper is in reality a thin felt of vegetable fibres, mechanically and chemically clarified, crushed, and torn into a pulp suspended in water. This pulp is spread equally in thin layers, drained, pressed, and dried into the compact substance we call paper.

Materials of Paper Manufacture.—The chief materials of paper manufacture are the waste rags from flax, hemp, silk, wool, and cotton. The linen rags are mostly in request for making the best and most durable white writing and printing paper. Silk and woollen rags are unfit for this purpose, as the bleaching material will not act upon animal substances. Cotton in a raw state requires less preparation than hemp. Rags are classed under different denominations—fines, seconds, and thirds, the latter comprising fustians, corduroys, stamps, or prints, as they are technically termed. The waste refuse from the wadding machine used in cotton spinning is employed for scribbling paper. Bibulous papers, such as blotting and filter papers, are made from woollen rags, on account of their open texture; cotton rags, also, make a spongier, looser paper when unmixed with linen.

Substitute for Rags.—The consumption of paper in Europe has more than doubled within the last fifty years, and, owing to the insufficient supply of rags, substitutes had to be found in straw and wood. The Chinese first used vegetable pulp for paper manufacture. The inner bark of the bamboo is particularly celebrated as affording a paper yielding the most delicate impressions from copper-plate, and this paper was originally called India-proof. The Chinese also use the bark of the mulberry and elm trees, hemp, rice-straw, and wheat. Among the straw species appears the maize (Indian corn), from the fibre of which a paper is made that for purity and whiteness cannot be equalled. Also the *Andropogon glycichylum*, or *Sorghum saccharatum*, a native of North America, is used. In fact, nearly every species of tough fibrous vegetable, and even animal, substance has been tried ; but of these straw has been most successfully applied, in combination with linen and cotton rags, when the silica contained in the straw is destroyed by means of a strong alkali. If the straw is not properly prepared the paper will be brittle and unfit for use. The use of straw is not very extensive, owing to the extra expense of preparation, and its waste under the process.

Esparto grass (the fibre of the *Macrochloa tenacissima*) and certain soft woods are very extensively used.

Straw, chopped up, is boiled with soda-lye in a revolving boiler, and is then washed

Red Colouring

Colouring Matter.	HCl.	H_2SO_4.	NaOH.
Orseilline B B. (Bayer & Co.)	Fibre violet-black, then black; liquid faint indigo.	Fibre black-blue; liquid indigo, reddish violet with water	Fibre violet; liquid reddish violet.
Congo red (Berlin Aniline Co.)	Dilute HCl: Fibre blue-black. Strong HCl: Liquid colourless	Fibre blue-black; dissolves dark blue on stirring.	Fibre scarcely changed.
Benzopurpurine I-B.	Dilute: Fibre red-brown; liquid colourless. Strong: Fibre dark brown.	Fibre black-blue; liquid do., on dilution red-black.	No action.
Benzopurpurine II-B.	Dilute: Fibre blue-black; liquid colourless.	Fibre black-blue; liquid dark blue, blue on dilution.	No action.
Delta purpurine G.	Dilute: Fibre brown-red; liquid colourless. Strong: Fibre greenish black.	Fibre blue-black; liquid dark blue, on dilution grey, then red-brown.	No action.
Delta purpurine 5B.	Dilute: Fibre red-brown. Strong: Fibre olive-black.	Fibre dark brownish olive; liquid dirty green, turning reddish on dilution.	No action.
Brilliant Congo.	Dilute: Fibre red-brown; liquid colourless. Strong: Fibre reddish black-violet.	Fibre blue-black; liquid blue, on dilution purple-violet.	No action.
Direct red.	Dilute: Fibre black-violet. Strong: Fibre blue; liquid colourless.	Fibre black-blue; liquid black-violet, grey-blue on dilution.	Fibre darker and rather bluer; liquid faint brown-red.
Naphthylene red.	Fibre dark black-green.	Fibre and liquid blue-black.	Scarcely any action.
Rosazurine B.	Dilute: Fibre dark purple-red. Strong: Olive-green.	Fibre and liquid dark blue, on dilution reddish, and then greenish.	No action.
Congo-Corinth.	Fibre black.	Fibre black; liquid dark blue, blue on dilution.	Fibre redder; liquid colourless; washing restores original colour.
Hessian purple N.	Dilute: Fibre black; liquid colourless.	Fibre black; liquid blue, on dilution grey-blue.	No action.
Hessian purple B.	Strong: Fibre dark grey, nearly black.	Fibre grey-black; liquid faint blue.	No action; liquid faint rose.
Azarine S.	Fibre gradually dark brown-red; liquid scarcely coloured. On dilution colour of fibre restored.	Fibre darker; liquid fine red; on dilution both yellow.	Fibre more blue; liquid bright cherry-red.
Azoeosine.	Fibre deep red-violet; liquid scarcely lilac. Water restores colour.	As with HCl.	Fibre dirty orange.
Carmosine.	Dilute: no action. Strong: Fibre deep red-violet; liquid faint lilac. Washing restores original colour.	Fibre violet-black; liquid the same.	Fibre rather browner; liquid light rose.

* All the colours unattacked by NaOH

Matters.

NH_3.	$SnCl_2$+HCl.	Alcohol.	Other Reactions and Remarks.
Like NaOH.	Fibre decol. slowly in cold, quickly boiling.	No action.	HNO_3: Violet spot, disappears on washing.
No action.	Fibre blue-black, then blue, then grey, then discharged.	No action.	HNO_3: Blue-black spot; red restored by NH_3. HNO_2: Fibre red-brown, colour not restored by NH_3; liquid becomes bluish red.
No action.	Fibre brown-red, then rose, then discharged.	Traces of colour extracted.	HNO_3: Fibre brown-black, Picric acid: Fibre red-brown.*
No action.	Fibre blue-black, then pale grey, then discharged.	No action.	HNO_3: Fibre-violet black, then more violet. Picric acid: Fibre dark brown
No action.	Fibre dark brown, then lighter, then rose, lastly discharged.	No action.	HNO_3: Fibre violet-black; violet red with NH_3. Picric acid: Fibre brown-red.
No action.	Fibre cinnamon brown, then slowly discharged.	A little colour extracted.	
No action.	Fibre red-brown, then discharged.	Trace of colour extracted.	HNO_2: Fibre black; with NH_3 black-violet. Picric acid: Fibre brownish.
Fibre fiery red; liquid scarce reddish.	Discharged.	No action.	HNO_2: Fibre red-brown; not changed by NH_3. Picric acid: A brown spot.
Extracts dye slightly that change of colour.	Fibre black, then grey, then discharged.	Liquid faint rose.	HNO_3: Blue spot with green margin. HNO_2: Fibre yellow-brown; NaOH turns the washed fibre dark brown; liquid light brown.
No action.	Fibre deep purple-red, then discharged.	Some colour extracted, red.	HNO_2: Dark yellow-grey, red-brown on washing, and touching with NH_3.
Fibre redder; liquid pale rose.	Fibre black, then blue-grey, and discharged.	Liquid scarcely rose-coloured.	HNO_2: Fibre black-blue; turns dark magenta-red on touching with NH_3.
No action.	Fibre black, then colourless.	Liquid scarce coloured.	HNO_2: Fibre violet-black; dark red-brown with NH_3. Picric acid: Fibre brown.
Liquid pale rose.	Fibre reddish grey, then colourless.	No action.	HNO_2: Fibre dark violet; with NH_3 red-brown.
Like NaOH, but fainter.	Fibre yellow on boiling; liquid yellow.	Liquid scarce rose.	Smells of alizarine oil; ash contains tin. HNO_2: No action. HNO_3: Orange spots. If NH_3 is added to the yellow liquor with $SnCl_2$ and HCl, turns violet.
Fibre scarlet; liquid scarcely coloured.	Very slight action in cold; on heating fibre colourless, liquid colourless.	No action.	HNO_3: Brown spot, removed by washing.
Fibre unchanged; liquid rose.	Slight action in cold, discharged on boiling.	No action.	HNO_3: Violet-brown spot, removed by washing.

are strongly attacked by hot soap-lye.

Colouring Matters.	HCl.	H_2SO_4.	NaOH.
Rhodamine.	Fibre dirty brick-red; liquid colourless. Fibre restored by washing.	As with HCl.	Fibre rather darker and bluer; liquid colourless.
Primuline red.	Fibre dark red-brown; liquid faint red-brown.	Fibre black-violet; liquid dirty do., red on dilution.	Fibre dirty red-brown.
Alizarine S.	Fibre orange; liquid light orange.	Fibre orange-brown; liquid orange, yellow on dilution.	Fibre and liquid violet.
Alizarine S. (purple shade with bichromate).	Fibre brownish yellow; liquid yellow.	Fibre brown; liquid brown-red, yellow on dilution.	Fibre and liquid violet.
			Yellow Colouring
Quinoline yellow.	Fibre yellow; liquid colourless, colour restored by water.	As with HCl.	Fibre deeper yellow, then discharged, restored by H_2O.
Auramine.	Fibre nearly discharged; liquid colourless, yellow partly restored by dilution.	Fibre discharged; liquid colourless.	Fibre and liquid colourless, yellow colour partly restored by H_2O.
Chrysamine.	Dilute: Fibre pale yellow. Conc.: Fibre red-brown; liquid rose yellowed on dilution.	Fibre magenta-red; liquid red-violet.	Fibre dark orange; liquid scarcely coloured.
Chrysophenine.	Dilute: No action. Con.: Fibre black-violet liquid scarcely coloured.	Fibre brown, then deep violet; blue on dilution.	Fibre unchanged; liquid scarcely yellowish.
Hessian yellow.	Dilute: Fibre paler. Con.: Fibre black-blue; liquid violet.	Fibre deep violet; liquid red violet.	Fibre dark red; liquid light rose.
Brilliant yellow.	Dilute: No action. Conc.: Fibre dark yellow; liquid nearly colourless.	Fibre black-violet; liquid violet.	Fibre cherry-red; liquid scarcely rose.
Curcumine.	Dilute: No action. Conc.: Fibre dark violet; liquid nearly colourless.	Fibre black-violet; liquid fine violet; blue on dilution.	As in brilliant yellow.
Tartrazine.	Fibre more orange; liquid yellow.	Same as HCl.	Fibre more orange; liquid orange-yellow.
Citronine.	Fibre deep violet-red; liquid magenta on dilution.	Fibre deep-violet; liquid violet.	Fibre dirty green-yellow; liquid colourless, yellow with water.
Primuline yellow.	No perceptible action.	Fibre first brighter and deeper, then pale yellow.	Fibre brighter and more orange; liquid colourless.
Toluylen orange G.	Dilute: No action. Conc.: Fibre violet; liquid reddish, on dilution colour restored.	Fibre magenta-red; liquid not much reddened.	Fibre light orange-red; liquid scarcely coloured.
Toluylen orange R.	Dilute: Fibre more rose. Conc.: Fibre paler liquid yellow; on dilution rose.	Fibre yellowish; liquid yellow.	Fibre more orange; liquid colourless.
Primuline orange.	Fibre and liquid reddish brown.	Fibre orange-brown; liquid deep red.	Fibre dark red-brown; liquid nearly colourless.
Oriol.	Dilute: No action Conc.: Fibre dark red; liquid light red, yellow on dilution.	As with HCl.	Fibre orange-red; liquid colourless.

NH_3.	$SnCl_2$+HCl.	Alcohol.	Other Reactions and Remarks.
Fibre as with NaOH; liquid rose, fluorescent.	No action in cold; fibre dirty brown in heat; liquid faint rose.	Slightly fluorescent extract.	HNO_2: No action. NHO_3; orange spot removed by washing; bears hot soap-lye well.
No action.	Fibre slowly becomes light reddish brown.	No action.	HNO_2: No action.
Fibre fine deep red; liquid colourless.	Fibre gradually orange; liquid yellow.	No action.	Yellow colour of $SnCl_2$ solution turns violet with NaOH,
No action.	No action in cold, red brown on heating.	No action.	HNO_3: Orange spot.
Matters.			
Scarce any action.	In cold no action; liquid yellow on heating.	No action.	HNO_3: Deep yellow spot.
Fibre paler; liquid colourless.	Slowly discharged in cold, quickly on heating.	No action.	HNO_3: White spot; turning orange in the middle.
Fibre bright orange; liquid colourless.	Fibre dirty yellow, slowly discharged.	No action.	HNO_3: Brown spot, turning reddish grey
No action.	Fibre brownish yellow, then colourless.	No action.	HNO_2: No action. HNO_3: Violet spot.
Fibre dark orange; liquid faint orange.	Fibre pale yellow, then decolorised.	No action.	
As with NaOH.	Fibre dirty yellow, quickly discharged.	No action.	
As in brilliant yellow.	Fibre brownish yellow, then discharged.	No action.	
As with NaOH, but fainter.	Discharged on heating.	No action.	HNO_3: No action.
Fibre unchanged; liquid colourless.	Fibre yellowish brown, discharged on heating; liquid yellowish.	Slowly extracted.	HNO_3: Violet red spot, then red in the middle, violet on margin
No action.	Faint action.	No action.	HNO_2: Fibre deep orange; with NH_3, orange-brown; red with β-naphthol.
No action.	Fibre more rose, discharged on boiling; liquid colourless.	No action.	HNO_2: Fibre grey; with NH_3, turns dirty yellow.
No action.	Fibre first rose, slowly discharged on boiling.	No action.	HNO_2: Fibre lilac-grey; more reddish with NH_3. HNO_3: Red violet spot turning grey.
No action.	Fibre orange-brown, then colourless.	Slight extraction.	HNO_3: Red-brown spot.
Fibre orange; liquid nearly colourless.	Fibre faint yellow, by degrees discharged; liquid colourless.	No action.	HNO_2: No action. HNO_3: Faint orange spots, fast to light.

Colouring Matter.	HCl.	H_2SO_4.	NaOH.
Croceine orange.	Fibre reddish brown; liquid rose.	Fibre darker; liquid orange; fibre colour restored on washing.	Fibre orange-brown; liquid nearly colourless.
Anthracene (derived from a vegetable colour).	Fibre rather greener; liquid also. Fibre and liquid colourless on watering.	As with HCl.	Colour deeper yellow; liquid pale yellow.
Xanthaurine (derived from vegetable colour).	Like anthracene.	Like anthracene.	Like anthracene.
Galloflavine (yarn dyed with alum tartar and $SnCl_2$).	Fibre darker; liquid yellow; both nearly colourless on dilution.	As with HCl.	Fibre more orange; liquid yellow.
			Green Colouring
Resorcin green.	Fibre yellow-grey; liquid orange-red.	Fibre and liquid; brown no change on dilution.	Fibre darker; liquid colourless.
			Blue Colouring
Victoria blue.	Fibre blue-black; liquid reddish; on dilution fibre green, then blue.	As with HCl.	Fibre dark red; liquid colourless.
Azo blue.	Dilute: No action. Conc.: Fibre black-blue; liquid colourless.	Fibre blue-black; liquid blue.	Fibre cherry-red; liquid faint rose.
Benzoazurine.	Fibre blue-black; liquid colourless.	Fibre black-blue; liquid greenish blue.	Fibre dark crimson; liquid rose.
Basle blue.	Fibre dark grey; liquid yellow; fibre blue on washing.	Fibre blue-black, then green, then yellow; liquid yellow. With water both blue.	Fibre darker.
New blue.	Fibre reddish violet.	Fibre dark grey; liquid grey.	Fibre violet-brown; liquid pale rose.
Nile blue.	Fibre green, then orange; liquid orange.	Fibre and liquid brown-red; on dilution yellow, green, and then blue.	Fibre red; liquid rose.
Naphthylene blue G.	Fibre brown-violet; liquid brown-orange.	Fibre black-brown; liquid dark brown, on dilution dirty blue.	Fibre brown; liquid orange-brown.
			Violet Colouring
Fast violet.	Fibre dark blue-black; liquid faint bluish.	Fibre black; liquid grey-blue; on dilution greenish, then red; fibre violet.	Fibre black-blue; liquid pale violet.
Azo violet.	Dilute: Fibre blue. Conc.: Fibre black-blue; liquid colourless.	Fibre dark blue; liquid blue-green.	Fibre crimson; liquid colourless.
Hessian violet.	Fibre dark blue; liquid nearly colourless.	Fibre dark violet-blue; liquid black-blue, on dilution blue-violet.	Fibre redder; liquid colourless.

NH_3.	$SnCl_2$+HCl.	Alcohol.	Other Reactions and Remarks.
No action.	Little action in cold; quickly discharged on boiling.	No action, or faint orange tint.	HNO_3: Black-blue spots.
Fibre unchanged; liquid scarcely yellow.	Fibre and liquid rather paler; no discharge on boiling.	No action.	HNO_3: Brown spot, lighter in middle. Fe_2Cl_6: Fibre and liquid olive-green. Alum does not give the fluorescence of fustic.
Like anthracene.	Like anthracene.	Like anthracene.	(Anthracene and xanthaurine both from Persian berries?)
Fibre darker and more olive; liquid almost colourless.	No particular action.		Heated with Fe_2Cl_6: Fibre dirty olive.
Matters.			
No action.	Slight discharge; liquid brownish.	No action.	HNO_3; Yellow-brown spot. Ash contains iron.
Matters.			
Fibre black-blue; liquid colourless.	Fibre darker in cold, green-blue on boiling; liquid green in heat, light blue when cold.	Slight extraction in cold, abundant on boiling.	HNO_3: Black spot, turning red-brown; turned brown-yellow by NH_3; latter colour permanent on washing.
Fibre violet-red; liquid rose.	Fibre black-blue, then slow discharge.	No action.	Picric acid: Colour blackish brown.
Fibre deep violet; liquid cherry-red.	Slow discharge.	No action.	Liquid turned deep blue by boiling with soap-lye.
No action.	No action.	Liquid very faint blue.	HNO_3: Black spot.
As NaOH.	Fibre green, then colourless; liquid colourless, blue on exposure to air.	Liquid faint blue.	
Fibre violet.	Fibre green, then colourless; liquid colourless, blue on exposure.	Liquid faint blue.	HNO_3: Yellow spot, green in middle.
Fibre brown-violet; liquid light red.	Fibre and liquid colourless.	Liquid very faint violet.	Vapour of HCl turns the blue to chocolate-brown (colour better for printing than dyeing).
Matters.			
Fibre unaltered; liquid very pale violet.	Fibre discharged, quickly on boiling.	Liquid scarcely violet.	HNO_3: Blue-black spots.
Fibre dark violet; liquid a faint magenta.	Discharged slowly.	No action.	Picric acid: Fibre black; turns blue with dilute acetic acid.
No particular action.	Fibre blue, discharged by prolonged boiling.	No action.	HNO_2: Dirty violet-grey; turned dirty red by NaOH. HNO_3: Large spot with pale blue margin.

Colouring Matter.	HCl.	H_2SO_4.	NaOH.
Heliotrope.	Dilute: Fibre dark violet. Conc.: Fibre black-blue; liquid light blue, violet on dilution.	Fibre black-blue; liquid blue.	Fibre dark crimson; liquid colourless.
Acid violet 7B.	Fibre green; liquid yellowish brown, green-blue on dilution.	Fibre blackish, then brown and brown-red; liquid brown-red, on dilution green-blue.	Fibre discharged; liquid colourless.
Gallocyanine.	Fibre and liquid violet.	Fibre dark blue-black; liquid intense Prussian blue, light magenta on dilution.	Fibre black-violet; liquid dirty purple.
Muscarine.	Fibre blue-black; liquid dirty blue.	Fibre green-black; liquid greenish, on dilution dirty violet.	Fibre brownish black; liquid nearly colourless.
			Brown Colouring
Benzo brown.	Dilute: Fibre reddish brown. Conc.: Darker; liquid purple-red.	Fibre and liquid black-brown.	No action.
Anthracene brown.	Fibre paler and yellower; liquid brown-yellow.	Fibre paler and redder; liquid chestnut, yellow on dilution.	Fibre black; liquid grey.
Fast brown R.G.	Fibre dark violet-red; liquid violet, colour restored on dilution.	As with HCl.	Fibre bright crimson; liquid cherry-red.
			Black Colouring
Cachou de Laval.	Fibre little changed; liquid faint grey.	Fibre rather yellower, especially after washing.	No action.
Alizarine black.	Fibre unchanged; liquid faint greenish blue.	Fibre and liquid as with HCl.	Fibre unchanged; liquid faint blue.
Brilliant black.	Fibre unchanged; liquid faint violet-red.		Fibre more greenish, liquid violet-black.
Naphthol black.	Fibre unchanged; liquid reddish.	Fibre unchanged; liquid olive-green.	Fibre unchanged; liquid scarcely reddish.
Resorcin black.	Fibre yellow-grey; liquid orange-brown.	Fibre and liquid brown.	Fibre unchanged; liquid very faint green.
Wool black.	Fibre unchanged; liquid light blue, rose on dilution.	As with HCl.	No action in cold; on boiling, fibre and liquid violet.

with hot water, the mass being then comminuted in a stuff-mill and bleached with chloride of lime whilst still hot. According to the statement of Lahkusse, 200 kilos. straw, 26 kilos. caustic soda, and 10 kilos. chloride of lime are required for the production of 100 kilos. of bleached, air-dried straw-stuff.

The root-cuttings of jute are also used in the manufacture of paper, as also the waste from rope-making, which serves for an inferior paper for envelopes.

Mechanical wood-stuff was first obtained by F. G. Keller, in 1840, by grinding wood

NH_3.	$SnCl_2$+HCl.	Alcohol.	Other Reactions and Remarks.
No particular action.	Fibre dark grey, then discharged.	No action.	HNO_2: Fibre green-grey, orange brown on washing and treatment with NH_3; liquid faint brown. Picric acid: Dark brown.
Like NaOH.	Fibre green; liquid blue-green; both blue on dilution.	Liquid scarcely violet.	HNO_2: No action. HNO_3: Olive, then dirty yellow; washing does not restore colour.
Like NaOH, but fainter.	Fibre turns yellowish grey; liquid colourless.	No action.	HNO_2: Fibre dirty violet-grey; liquid blue-green, green, and then yellow.
Fibre violet-blue; liquid scarcely violet.	Fibre blackish, blue on heating, then green and yellowish grey.	No action.	HNO_3: Black spots. (Probably formed by action of a nitroso compound upon a dioxynaphthaline).
Matters.			
No action.	Colour yellower and lighter; liquid brown-yellow.	Extracts traces of of colour.	Resists light badly.
Fibre brown-grey; liquid nearly colourless.	Fibre brown-yellow; liquid the same.	Extracts traces of colour.	HNO_3: Black spot.
As with NaOH.	Darker at first, then discharged.	No action.	HNO_3: Black spot, turning light red-brown.
Matters.			
No action.	Fibre more reddish or brownish.	No action.	Goods are rarely dyed with cachou de Laval alone. When topped with other colours, it is difficult to detect.
No action.	On boiling, brownish.	No action.	HNO_3: A dark olive spot.
Fibre unchanged; liquid violet-black.	Fibre dark garnet on boiling; liquid colourless.	No action.	HNO_3: Dark red-brown spot.
No action.	On boiling, fibre light green, blue on washing.	No action.	HNO_3: A brown spot. (A mixture of various colours.)
No action.	Fibre and liquid light brown.	No action.	HNO_3: Yellowish brown spot. Ash contains iron.
No action.	Fibre discharged.	No action.	HNO_3: Light red-brown spot.

under millstones. This article only obtained industrial importance in 1846, by the introduction of suitable machinery for its comminution and sorting, which rendered possible the production of a uniform quality on the large scale. Ground wood serves for the production of inferior papers, as its fibre is too short for strong papers and not susceptible of felting. Hence it serves more for filling up than as a substitute for rags. The resin present resists the action even of a strong bleach. Paper from ground wood (mechanical wood-stuff) readily turns yellow.

Much more important is the chemical production of cellulose, for which the wood of coniferous trees is chiefly used. The stems, freed from bark, branches, &c., are cut up and boiled from two to three hours in wrought-iron vessels in caustic soda-lye of sp. gr. 1·085 under a pressure of from 6 to 10 atmospheres. The whole is then run off into cisterns, where the brown lye escapes at the bottom. The soda is recovered by evaporating down the liquid and igniting the residue. The fibrous mass is lixiviated with water and washed clean. The oil of turpentine evolved is sometimes collected in suitable refrigerators. The recovery of vanilline, the presence of which is detected by the odour, has been attempted unsuccessfully. The bleaching is effected in the hollander.

From a calculation given by the author, it appears that, at German prices, 1 ton of wood cellulose costs only 240 marks, whilst the same weight of esparto cellulose costs 305·6 marks.

Sulphurous acid is also used in the production of cellulose. The comminuted wood is treated under pressure with an acid solution of calcium sulphite obtained by placing pieces of calcium carbonate in a tower and passing over them water from above and sulphurous acid from below. The wood, cut up and freed from bark, is steamed in a boiler lined with lead, into which the acid solution of calcium sulphite is introduced. The whole is heated first to 108° and then gradually raised to 118°. If a sample of the liquid is mixed with ammonia the residual calcium sulphite falls to the bottom, but the salts formed during the working of the process are not precipitated. The proportion of the effective solution can easily be determined from the precipitate. If the precipitate is only about $\frac{1}{16}$ of the volume of the sample, the time for boiling off the sulphurous acid is arrived. The temperature and the pressure sink simultaneously. If the precipitate in the test-glass is only $\frac{1}{32}$ in bulk, the process is completely at an end and the solution must be quickly run off. A higher temperature would hasten the process, but would require a higher pressure, and the cellulose obtained would be inferior in both quality and quantity.

The chemical process which takes place during boiling is, according to Mitscherlich, as follows:—The sulphurous acid is oxidised to sulphuric acid by a part of the oxygen of the organic matter, and this acid under normal conditions combines with the bases, which were previously combined with the sulphurous acid. If the process is mismanaged, free acid is formed in the solution. At the same time tannic acid is formed from the incrusting substances. For the right management of the process a main condition is that the sulphurous solution must be free from polythionates, as the operation miscarries in presence of the latter. At the same time the temperature increases rapidly, and samples drawn show an anomalous decrease of sulphurous acid. The polythionic acids generally appear in consequence of the presence of free fumes of sulphuric acid during the roasting process. To avoid this, care must be taken that the sulphurous acid is free from sulphuric acid or its salts.

Ekman boils with a solution of magnesium sulphite produced by exposing calcined magnesia in towers to the action of sulphurous acid and of water. He boils, *e.g.*, esparto grass (freed from roots, &c.) with a solution of 1–4 per cent. magnesia and 4–5 per cent. sulphurous acid. After the pressure has gradually been raised to 5·75–6 atmos., and is kept at this point for from two to four hours, fibres are obtained which, after being well washed, are at once fit for common printing paper, and for better sorts after bleaching with chloride of lime.

An experiment made at Bergvik gave the following results:—Of the 4395 kilos. of deal planks used there appeared by the removal of branches a loss of 260 kilos.; by cutting, sorting, and dusting, &c., of 565 kilos., or a total loss of 825 kilos. The remaining 3570 kilos. were placed in four boilers, and yielded, after washing in common

hollanders, 2875 kilos. of stuff, equivalent to 1437 kilos. of dry stuff, or 32·68 per cent. of the crude wood, which contained 21 per cent. of moisture.

In comparing the results of the various sulphite processes, the test for lignose with aniline sulphate is not trustworthy. It is better to treat the products with chlorine, after which the lignose substance is turned a magenta colour by sodium sulphite. The remaining lignose may be quantitatively determined by boiling with potassa-lye. According to Christy, in Ekman's process the incrustations are completely dissolved, so that the washed stuff gives no colour with aniline sulphates, and dissolves in sulphuric acid almost entirely without a dark coloration. Fig. 573 shows the fibres of the white pine (*tanne*) in a longitudinal section, and Fig. 574 in a cross section as it appears under the microscope after treatment by Ekman's process. Fig. 575 shows the fibres (strongly attacked) of linen (L) and cotton (B) rag papers. Fig. 576 shows ground wood from conifers, with the cells and pith radii, which are here easily recognised, whilst in

Fig 573.



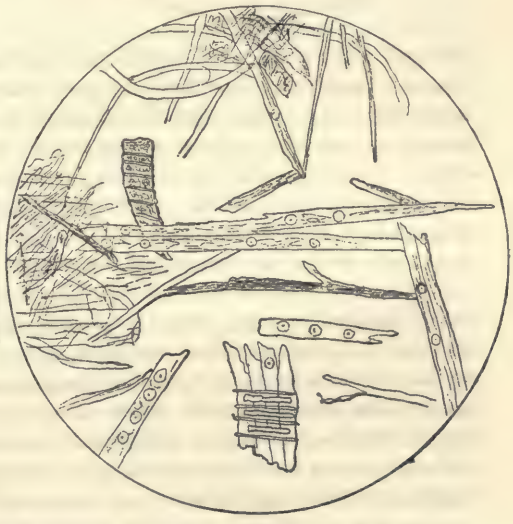
Fig. 574.



Fig. 575.



Fig. 576.



chemical cellulose (Fig. 577) they are not easily recognised. Fig. 578 represents straw-stuff, with its cells, 0, very distinct from those of esparto.

In examining wood and other fibrous vegetable matter, H. Müller boils 5 grammes of the sample five times, using each time 100 c.c. of water. He dries and weighs them, and then treats them in a lixiviating apparatus with a mixture of alcohol and benzene, to dissolve fat, wax, resin, &c. Colouring matter and pectosic substances are removed by repeated boiling with dilute ammonia. For obtaining the cellulose in a state of purity the sample is covered with 100 c.c. water in a wide-necked stoppered glass, and then, according to the nature of the sample, there are added from 5 to 10 c.c. of a solution of bromine containing 2 c.c. bromine in 500 c.c. water. The yellow colour of the liquid disappears gradually on treating the purer bast-fibres, such as flax or hemp, but

in a few minutes in straw-stuffs or woods. When the colour has disappeared a fresh quantity of the bromine solution is added, and so on, until at last a point is reached when the absorption becomes so sluggish that the liquid remains yellow even after the lapse of from twelve to twenty-four hours, and the presence of free bromine can be

Fig. 577.

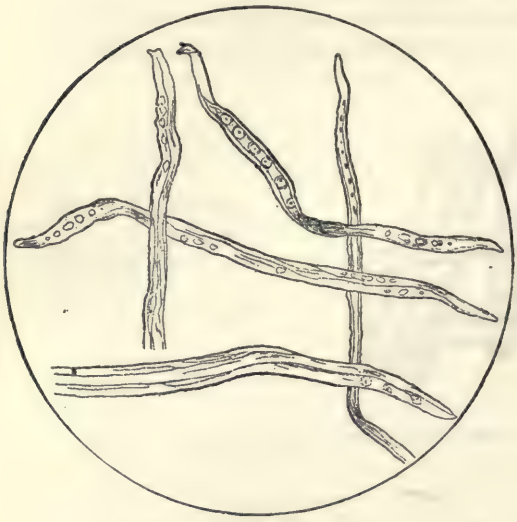
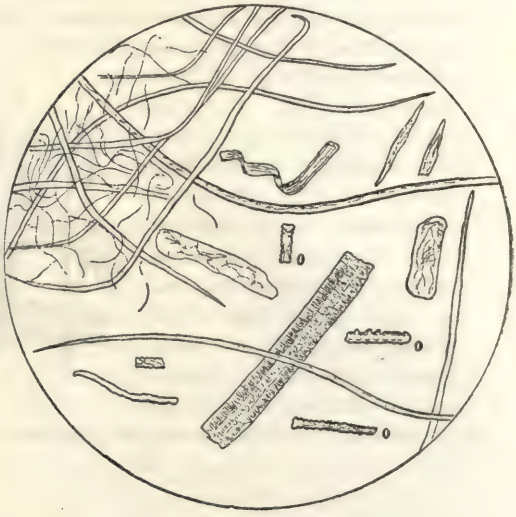


Fig. 578.



detected. The mass, when freed from the liquid by filtration, is washed with water, and heated almost to a boil with 500 c.c. of water, to which 2 c.c. of liquid ammonia have been added. All crude vegetable fibres and woods, without exception, if thus treated, take a more or less intense deep brown colour, as does also the liquid. The filtered and washed mass is returned to the stoppered glass, again covered with water, and solution of bromine is again added. The first addition of bromine is generally easily absorbed, and the dark colour becomes lighter. The purer fibres, to which only quantities of 5 c.c. are added in the second treatment, soon become colourless, and if further quantities of bromine are added, they remain unabsorbed for days. On the other hand, lignified tissues, after the above-mentioned treatment with ammonia, absorb bromine with undiminished readiness, and we may continue adding quantities of 10 c.c. of the bromine solution until the absorption comes to an end. When this point is reached the treatment with dilute ammonia is repeated. With the purer fibres this second treatment is usually sufficient, but more strongly lignified tissues require a third and sometimes a fourth treatment with bromine in gradually reduced quantities. After drying and weighing the cellulose, the quantity of the soluble modification of cellulose can be approximately determined by the loss on boiling four or five times, each time with a solution of 1 part crystallised sodium carbonate in 100 parts of water. Such soluble cellulose is probably in most cases wasted in the technical treatment of fibrous materials.

The nitrogenous material derived from the protoplasmic contents of the cells, which are partly soluble and partly insoluble, are small in quantity, and their presence has no technical importance.

In many raw materials an important part of the cellulose occurs in the state of worthless tissues, and it is then important to know its proportion. As this is not practicable chemically, it has to be reached by mechanical means. An approximate separation may be reached by stirring up the cellulose with an abundance of water, and pouring it upon a straining-cloth, stretched over a funnel, repeating this treatment

as long as the water runs through turbid. In this manner the following figures were obtained:—

Woods.	Water.	Watery Extract.	Resin.	Cellulose.	Incrusting Matter.
Birch	12·48	2·65	1·14	55·52	28·21
Beech	12·57	2·41	0·41	45·47	39·14
Oak	13·12	12·20	0·91	39·47	34·30
Alder	10·70	2·48	0·87	54·62	31·33
Lime	10·10	3·56	3·93	53·09	29·32
Chestnut	12·03	5·41	1·10	52·64	28·82
Fir	12·87	4·05	1·63	53·27	28·18
Poplar	12·10	2·88	1·37	62·77	20·88
Pine	13·87	1·26	0·97	56·99	26·91
Willow	11·66	2·65	1·23	55·72	28·74

According to F. Schulze, 1 part of the dried and pulverised material is extracted first with water, then with alcohol and ether, and after it has been well dried it is treated for from twelve to fourteen days, at a temperature not exceeding 15°, with 0·8 part potassium chlorate and 12 parts nitric acid of sp. gr. 1·10. After the lapse of this time it is diluted with water, filtered, and washed, first with cold and then with hot water. The contents of the filter are rinsed into a beaker and digested for three-quarters of an hour with weak ammonia (1 part to 50 water) at about 60°. The mass is then washed with cold ammonia until the filtrate runs through colourless. It is then successively and completely washed with cold and hot water, with alcohol and ether. If we disregard a small trace of nitrogen, the cellulose so obtained is chemically pure.

If wood is treated with soda-lye at elevated temperatures and high pressure, a relatively large part of the cellulose is dissolved and wasted.

As a reagent for wood Friesner recommends phloroglucine. If a paper contains ground wood-stuff it turns violet red, if first moistened with HCl and then with phloroglucine. When lignose is mixed with cellulose the test is uncertain, and a miscroscopic examination is required.

Mineral Additions to Rags.—A moderate addition of a mineral body to the paper material whitens the whole, and for inferior or ordinary paper it is successfully employed. It is unfit for very thin paper, making it shiny and brittle. A profitable addition of mineral matter is from 5 to 10 per cent. of the weight of paper, a greater addition making the paper dull, brittle, and hairy to write upon. The usual mineral mixtures in frequent use at the present day are—clay free from sand, china clay, or kaolin. Annaline pearl-hardening, in the form of a pulp resembling clay, is most preferred, being not so expensive. In 1850 it was favourably received, under the names of fixed white, raw white, patent white, or permanent white. 15 kilos. of the paste with 100 kilos. of paper pulp are generally employed.

Precipitated barium sulphate has been latterly much used in paper-making, as have also finely-ground bauxite and precipitated magnesia.

Manufacture of Paper by Hand.—The old method of making paper by hand was from the pulp of waste paper placed in a mould of the required size; but this method, although still used for writing paper, was found to restrict the size of the sheets, and different methods were tried with varied success, until a machine was invented which, without the aid of moulds, manufactured the paper in any length.

Cutting and Cleaning the Rags.—The Cutting and Sorting of the Rags.—The first operation is performed by two machines, called the half-hollander and the whole-hollander. The rags are next treated chemically with potash to rot them. By the old method, rags were cut into pieces about four inches square, by being drawn across a sharp knife fixed upon a table. Machinery has superseded this arrangement, and various cutting machines have been invented, among which we may mention that of

Davey, in which a horizontal knife revolves around a fixed cylinder cutting the rags into strips. Bennet's cutting machine consists of two knives radiating from a wheel, and bearing against another knife. Some machines are constructed with a quantity of circular sharp-edged steel plates, like the machine of Uffenheimer, of Vienna. After cutting, the rags are cleansed from dust and other impurities by the Willow machine. The best kind of sifting machine is in the form of a drum with the upper part covered with a wire grating. The rags are put in by a side door, which acts, as the drum revolves, as a refuse door, casting off the sand and impurities, leaving the rags winnowed. They are next boiled in an alkaline lye, or solution of 4 to 10 lbs. of sodium carbonate, with one-third of quicklime to 100 of the material. The rags are placed in large cylinders slowly revolving, and causing them to be constantly turned over. Into these cylinders a jet of chlorine water, with a pressure of 30 lbs. to the square inch, is directed. H. Volter patented in 1859 a horizontal steam cylinder, which receives the steam from a tubular guide-cock provided to the boiler, an inner cylinder revolving to move the rags. The distant end of the boiler and the tubular cylinder draws up, and the mass is easily poured into the washing machine when in a fluid state (Silberman's Washing Hollander). Although partly cleansed by the above method, the rags still require further boiling.

The Separation of the Rags for Half-stuff and the Whole-stuff.—The machine used in separating and rending the rags are :—

1. The German stamping machine.
2. The rag mill (rolling hollander).
 (α) The half-hollander.
 (β) The whole-hollander.

Formerly the rags were rotted before crushing, being placed in a stone trough, where in two or three days they became heated, and developed a strong ammoniacal odour. When the surface was covered with a mould, the rags were sufficiently decayed for the purpose of manufacture. They were then taken out in a brown mass, those remaining behind as sediment being used for coarse paper. The present method of boiling the rags with alkalies is preferable, giving the paper greater firmness.

Stamp Machine.—The German stamp machine is at the present time only to be found in smaller manufactories. It is of the nature of a hammer. Six or eight stamp rods are fixed into a strong oak beam, and work intermittently with a set below. Through an opening provided with a fine sieve the water is conveyed away. As the hammers rise and fall, the stamp holes serve for a water conduit. Three to five hammers work in each hole. The rags are mixed with sufficient water to form a pulp, and remain in the machine twelve to twenty hours.

The hollander has a cylinder set with blades or knives and kept in rapid rotation. Below this is the so-called ground-work fitted with similar blades. After the chest has received the necessary quantity of water the rags, &c., are thrown in. The roller is set in motion with a speed of from 100 to 150 rotations per minute. The blades strike into the liquid and draw the rags into the space between the circumference of the roller and those of the ground-work—the two sets of knives acting like the blades of scissors—and finally eject the mass in a state of fine division over the steep slope of the cran.

Bleaching the Pulp.—After this the mass is placed in another machine, the whole-hollander, and bleached by a solution of chloride of lime, chlorine water, chlorine gas, or other bleaching agent. The lime is retained in the machine until the rags are sufficiently bleached; the pulp is then let down into long slate cisterns to steep before placing in the beating machine.

When bleached by chloride of lime, 1 to 2 kilos. are applied to 100 kilos. of pulp.

When greater smoothness is required, a little hydrochloric or sulphuric acid is added, although care must be taken in its use, for applied too largely it destroys the fibre. Orioli employs aluminium hypochlorite, known by the name of Wilson's bleaching preparation, aluminium chloride being obtained on the one hand, while, on the other, all the bleaching effects arise from the delivery of ozonised oxygen,

$$Al_2Cl_6O_3 = 3O + Al_2Cl_6.$$

Varrentrapp's zinc hypochlorite, under the name of Varrentrapp's bleaching-powder, is worthy of notice as being extensively used. In this powder, chloride of lime, decomposed with zinc vitriol, or, better, with zinc chloride, is employed. When bleached by zinc chloride, the mineral acid decomposes the chloride of lime, therefore no risk is incurred by the fibre.

Antichlore.—When the bleach retains chlorine, it is washed in soda, potash, or antichlore, to neutralise the adhering hydrochloric acid, which merely washing in water would not effect. The chief constituents of antichlore are sodium sulphite, tin chloride, and sodium hyposulphite. A mol. of sodium sulphite ($Na_2SO_3 + 7H_2O$) removes 1 mol. of chlorine (Cl_2), whilst hydrochloric acid and sodium sulphate are formed. A mixture of sodium sulphite with sodium carbonate is employed to neutralise the hydrochloric acid. The sodium sulphate and sodium chloride are removed by washing. Calcium sulphite is greatly approved, and is considered to be as effective as antichlore, when applied as the corresponding sodium salt. A mol. of tin-salt ($SnCl_2 + 2H_2O$) is taken up by a mol. of chlorine (Cl_2), by which tin chloride ($SnCl_4$) arises. After the working is completed, so much sodium carbonate is added as is required to saturate the hydrochloric acid. A mol. of sodium thiosulphate ($Na_2S_2O_3 + 5H_2O$), absorbs 4 mols. of chlorine, whilst sodium sulphate, hydrochloric and sulphuric acids are formed.

Blueing.—Notwithstanding careful chemical bleaching, the pulp has still a yellow tinge, and requires a colouring matter which is generally introduced in the process of beating. The blues commonly used are ultramarine, Paris blue, indigo, aniline blue, and oxide of cobalt. With 100 kilos. of the dry paper stuff, 0·5 to 1·5 kilo. of ultramarine are mixed, according to the strength of the colour required.

Sizing.—The pulp requires sizing to preserve the colour. It is guided, as it issues from the hollander, through a tub of size, and afterwards carried over skeleton drums, containing revolving fans to dry it as it passes; heated cylinders are also used for drying. Starch is used to give a thicker consistence to the size, which is generally made from the best glue, resin being added in quantities never exceeding 3 kilos. per 100 kilos. of the pulp, to impart the desired amount of stiffness.

a. **Hand-made Paper.**—*Straining the Paper Sheets.*—There are three ways of straining or filtering the pulp:—First, by straining through a brass sieve with fine slits to allow the pulp to pass, and retaining all lumps and knots. Secondly, by pressure; and, thirdly, by evaporation. In the first operation the sheet is formed by a mould of the size required being dipped into a tub of pulp previously strained. The pulp becomes extended to a thin layer and the water filters off. The tub is either round or of a quadrangular shape made of wood, lined with lead. A broad board running across the tub is called the bridge, and a smaller one under the large one the little bridge. The large bridge has a pointed support, technically termed the donkey, for the form or frame to lean against.

The sifting machine, technically termed the knotter, used in the manufacture of hand-paper, consists of an upright cylindrical sieve, in which an inner cylinder revolves. As the whole-stuff is taken from the tub, the remainder becomes massed together, and steam or other pressure is employed to force the pulp through the sieve and cylinder, the latter retaining the lumps and knots. The paper forms, upon which the whole-

stuff is placed, are constructed with brass wires to allow the water to drain off, retaining the pulp. There are two kinds of forms:—

(1) The Ribbed Form.—A square or oblong frame of oak or mahogany with parallel brass wires and cross wires at intervals to steady them. Lined paper is made on this form, and is not much glazed on account of the time and expense, being reckoned an inferior paper.

(2) The Vellum Form.—A frame of fine brass wire-work. Vellum paper is made on this form, and has a delicate even surface; it can be made to present any degree of glossiness, by pressing and satining. When held to the light it appears uniform, not possessing bright and opaque lines as in the former paper.

A ribbed form similar to the vellum form is employed in the manufacture of paper distinguished by trade marks, coats of arms, &c., the impress of the wire forming what is termed the water-mark; bank-notes are made separately in a mould in this way. The edge of the form makes the edge of the paper, forms being used according to the size required; also the quantity of the whole-stuff varies in accordance with the required thickness of the sheets. Felt is extensively used in the manufacture of paper; it is unlike the ordinary felt for hats, being a coarser, looser, white woollen fabric, more suitable for rolling.

The work of the pulp-tub is divided into two parts, the squaring and the scooping; the latter is the placing of the pulp in the mould, the former the placing of the sheets between felt. The tub is stirred occasionally with a pointed stick, technically termed the scoop stick. The pulp is taken out on the form in a sloping position, shaken a little to aid cohesion, and finally placed on the small bridge. The next sheet is placed on the large bridge. The form is laid in a sloping position against the donkey-rest to drain, and the paper finally placed on the felt to dry a little, the empty form returning to the tub. The first paper sheet is covered with felt, on which the next is placed; the average number of sheets manufactured exceeding 5000 a day.

Pressing the Paper.—As soon as there is a sufficient number of sheets, they are made into a thick bale and placed under the press, the number of sheets comprising a bale being generally 181. Three bales, $181 \times 3 = 543$ sheets; twenty quires $= 480$ sheets sized, and 500 unsized. Pressing gives firmness and glossiness, and by continued pressing exceeding smoothness is obtained.

Drying the Paper.—The process of pressing has not quite removed the water from the paper, which has to be dried in an airy chamber, the sheets being placed separately, or two to five together as required. An expert workman can place from 800 to 900 layers of two to five sheets each in a day, as well as hang and dry the sheets and take them off the cord.

Sizing the Paper.—Paper is not durable unless it is sized, and is only used for filtering, packing, printing, or scribbling papers. Sizing gives the paper substance by filling the pores, and making it firmer, stiffer, and harder. Ordinary size dissolved in water will not always prove effective, and it is necessary to add a solution of an aluminium salt, such as that of alum, aluminium sulphate, or aluminium chloride, to prevent decay. Without chemical preparation the sheets are rendered sticky and have to be sized separately, but with the above addition from 80 to 100 sheets can be successfully sized by hand; a good workman can size from 40,000 to 50,000 sheets in twelve hours. The sheets must not be dried too quickly after sizing.

Preparing the Paper.—After the sized paper is pressed and dried, it requires further preparation to make it fit for use. The first process consists in the finishing or trimming to remove all the little specks and blemishes, and to smooth the sheets. The finished sheets are counted and placed together, the workman by continued practice counting 8000 to 15,000 sheets as he places them, and separating them into whole and half quires, twenty-four sheets of sized and twenty-five sheets of unsized

paper making a quire; the upper and under quire of each ream being placed on an extra sheet, known as *outsides*. The even and glazed surface is mostly obtained by hot-pressing, when every sized sheet is interposed between two unsized sheets; this is called *interchanging*. The preparation of the various kinds of paper is now accomplished, with the exception of the finest letter paper, which requires an extra process to give it a final gloss, by pressing between the rollers of the satining machine. The different varieties of paper are classed under three denominations:—

The Different Kinds of Paper.—A. Writing and drawing paper, the smaller kinds of copy paper, deed paper, the finer post and letter paper, and vellum letter paper.

B. Printing paper for books, as distinguished from copy printing, deed printing, post and vellum printing, note and copper-plate paper. Silk papers for fancy purposes ornamented with gold or silver, and printed from engraved copper plates.

C. The looser textured papers, such as unsized parcel paper; the better kinds are filter* and blotting-papers. Packing-paper is half-sized, and is met with as a yellow straw paper, blue sugar paper, and pin and needle papers.

β. **Machine Paper.**—*Manufacture.*—Manufacturing paper by hand requires much time and labour, and machinery is found to be quite as efficient. Endless paper of any breadth can be made by machinery with the same amount of strength and firmness as hand paper. The straight form and the vibrating machine are used for finer paper.

It is requisite that the machine should:

(1) Make the pulp of a suitable consistence by diluting it with water.

(2) Purify the whole-stuff from knots.

(3) When free from knots work the material by means of regulators, delivering the stuff from the form, and producing by the uniform flow of the pulp a smooth paper leaf of the breadth required.

(4) Be so regulated that the stream of whole-stuff may form a sharply turned leaf.

(5) Free the paper leaf from water, so that it only requires drying in an airy chamber and pressing.

(6) Remove the water, steam cylinders being principally used.

The finished paper is cut into sheets by the paper-cutting machine.

After the whole-stuff is thinned to a consistence easily moved by water, it flows to the knotter, placed in a perforated cylinder of sheet brass, which is supplied with an interior mechanism revolving with greater velocity. One of the best knotting machines is Manuhardt and Steiner's, of Munich. After the whole-stuff is purified by the knotting machine it passes out, and the whole-stuff reservoir is supplied anew. In course of time the consistence becomes altered, sometimes producing a thicker sheet than required. This variation is obviated by the regulator, an essential in the paper manufactory.

Hartig classifies papers as blotting-paper (unsized), printing-paper (sized with resin), draught-paper, letter-paper, paper for account books and legal documents, and covering paper, all the three better kinds being sized with a mixture of glue and resin-size, and lastly parchment paper.

For testing the strength of papers apparatus have been devised by Heuer, Rausch, and Wendler. Papers are also arranged in seven classes, according to their resistance to rubbing and crumbling. The position of a paper in this series is ascertained by certain manipulations, which can only be learned by practice.

Paper-Cutting Machine.—When finished by the machine, the paper is cut off into long lengths and rolled by hand for the manufacturers of drawing- and wall-papers,

* Filter paper should be free from soluble matter and from earthy, alkaline, or metallic compounds, being as near as possible chemically pure cellulose. The finest qualities are made in Sweden and in Germany.—[EDITOR.]

scene-painters, &c. Attached to a large wheel is a knife, whose regular strokes cut paper into the size required. The clipping machine is used for cutting the edges of books.

γ. **Pasteboard, &c.**—*Making Pasteboard.*—Pasteboard is made in three ways:

(1) By placing the pulp in a form—form-board.
(2) By placing several damp sheets to form a thick card—elastic pasteboard.
(3) By pasting together the finished paper sheets—sized pasteboard.

(1) Form-board is an inferior kind employed for ordinary purposes of packing, bookbinding, &c. It is made from waste paper, refuse rags, and the coarser parts of the pulp. Clay or chalk is sometimes present to 25 per cent. of the weight of this pasteboard. It is made in a coarse ribbed form, goes through the same process of knotting as the paper sheet, and is dried and pressed under a roller.

(2) Elastic pasteboard is of better material and presents a smoother surface; six to twelve sheets of paper previously damped are placed together, and pressed into one compact sheet. A separate and harder kind of pasteboard is the thick elastic board used for binding books. The inner layer is made of coarser stuff, sawdust, &c.

(3) Sized pasteboard, or cardboard, is made of two to fifteen sheets of sized paper, pressed, and satined. There are varieties of this cardboard, such as Bristol-board, and London-board, the former being extensively used for water-colour drawing, mounting-board, ornamental board, &c.

Papier-Maché is used for fancy articles, such as the covers for albums, inkstands, blotting-books, paper-knives, &c., as well as for the cells of galvanic batteries. It is obtained from old paper made into a pulp with a solution of lime, and gum or starch, pressed into the form required, coated with linseed oil, baked at a high temperature, and finally varnished. The pulp is sometimes mixed with clay, sand, chalk, &c., and other kinds are made of a paste of pulp and lime, and used for ornamenting wood, inlaying, &c.

Coloured Paper.—The papers made from coloured rags are the brown packing-paper and coarse coloured papers, such as sugar- and pin-paper. To 50 kilos. of dry pulp coloured pin-paper requires the several undermentioned substances:—

Yellow	2·05 kilos.	Lead acetate
	0·45 „	Potassium bichromate
Blue	2·05 „	Iron sulphate
	1·05 „	Potassium ferrocyanide
Green	3·00 „	Blue
	1·05 „	Yellow
Violet	1·05 „	Extract of logwood
Rose	6·00 „	Extract of Brazil wood
Buff	3·00 „	Oil of vitriol
	3·00 „	Chloride of lime

Ultramarine and aniline blue are also used in colouring the paper. In variegated papers, chemical, mineral, and vegetable colourings are used according to the required colours. Body colours are rendered fluid by a solution of gum arabic or alum in the size, which can be applied by a brush or sponge when only one side is to be coloured. Variegated and tapestry papers are an important part of the manufacture.

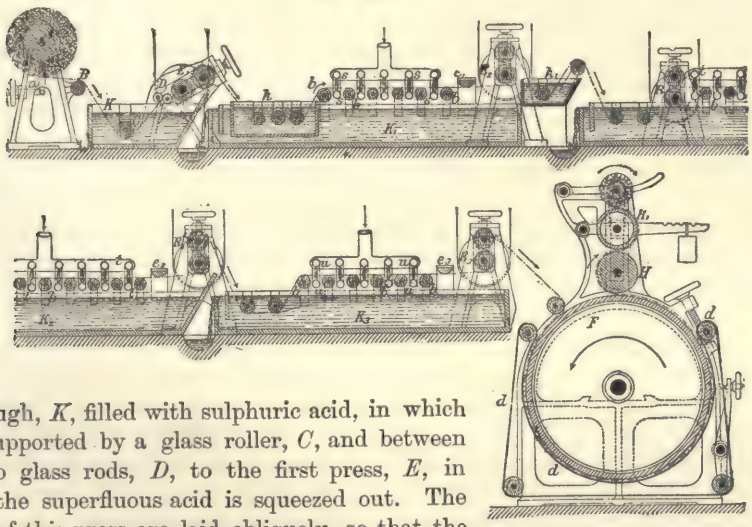
In the manufacture of coloured papers there are used solutions of mineral or organic colours, prepared according to the rules of dyeing, and fine earthy colours are stirred up with starch-paste or with solutions of gum, dextrine, or glue mixed with alum. If only one side of the paper is to be coloured, the colour is applied with a brush or sponge. Otherwise the sheets are taken at once through the liquid. In the manufacture of paper-hangings the processes are similar to those employed in calico-printing. This manufacture is now very important.

Graphite paper, used for packing up needles, and other small and fine articles of iron or steel, with a view of preventing rusting, is prepared by hand with an addition of finely powdered graphite.

Parchment Paper.—Parchment, although made of animal membranes, is often confounded with vegetable parchment (*phytopergament*). The latter is made of unsized paper treated with a solution of chloride of zinc or sulphuric acid: 1 kilo. of concentrated sulphuric acid and 125 grammes of water, in which the paper is immersed so as to equally affect both sides. The length of time differs according to the quality of the paper, the thicker or firmer paper taking a longer time to saturate; soft paper will take five to ten seconds. It is then placed in a weak solution of sal ammoniac, rinsed in water till no trace of the acid remains, and then dried. When these operations are effected mechanically, a steam machine first pulls the endless paper through a vat of sulphuric acid, then through water, sal ammoniac, and again water, the paper passing on over cloth rollers to dry, and finally over polished rollers to press and glaze the surface.

In Fritsch's machine for parchmentising paper, the paper travels from the cylinder *A* (embraced by the beak, *a*, Fig. 579, to regulate its tension), over the roller, *B*, into

Fig. 579.



the trough, *K*, filled with sulphuric acid, in which it is supported by a glass roller, *C*, and between the two glass rods, *D*, to the first press, *E*, in which the superfluous acid is squeezed out. The rollers of this press are laid obliquely, so that the acid pressed out may quickly flow back into the trough, *K*, without flowing along the paper. From *E* the paper passes into a chest, *k*, filled with water, and fixed in the large tank, *K*, in order to wash off the acid adhering to the paper. The water remains in *k* until it marks about 30° Tw., and is then let off to recover the acid, whilst its place is taken by fresh water. The paper is passed over a row of wooden rollers, *b*, and is rinsed from above and below with fresh water from the spirting tubes, *s*, in order to arrive after the expander, *e*, at the second press, E_2, when the dilute acid or the gelatinous coating is pressed out. The paper next passes through the trough, K_1, filled with an alkaline bath, in order to neutralise any adhering acid, and for its second and third washings respectively to the trough, K_2, with the spirting tubes, *t*, and the trough, K_3, with the spirting tubes, *u*. After a passage through the third press, E_3, the paper is passed upon the drying cylinder, *F*, heated by steam, round which it is held by an endless felt, *d*. Above the drying cylinders are placed the smoothing rollers, *H*, H_1, the upper one of which, H_1, is heated to prevent sweating and the formation of rust-stains. The finished parchment paper is then rolled up. For the press rollers, E_1, E_2,

and E_3, there are used so-called anti-deflection rollers, which are coated with a layer of caoutchouc. The presses are set in action by expansible band discs.

If dipped in water parchment paper becomes soft and limp without losing its firmness. It is permeable for liquids only by dialysis. It is not attacked by boiling, and does not putrefy. From its valuable properties parchment paper is suitable for a variety of purposes, especially as a material for deeds, official documents, &c., and indeed for all writings the preservation of which is important. In comparison with ordinary parchment it is much less liable to be destroyed by insects. It is used in bookbinders' work, and as a substitute for leather—*e.g.*, the so-called "sweat-leathers" in hats and caps. It is used instead of animal bladder for covering glasses of preserved fruits, and for connecting the joints of distillatory, &c., apparatus. It may be cemented together by means of cellulose dissolved in cupric ammonia. According to Ludicke in the conversion of paper into parchment paper the thickness of the paper decreases from 35 to 37 per cent. Its density increases from 32 to 42 per cent. and it increases in firmness 3·8 to 4·5 fold.

SECTION VIII.

MISCELLANEOUS ORGANO-CHEMICAL ARTS AND MANUFACTURES.

TANNING.

THE operation by which the skins of various animals, more especially those of the larger mammalia, are converted into leather is called tanning. By leather we understand a substance, tough, flexible, not harsh; further, distinguished by resisting putrefaction and by not yielding any glue when boiled in water, as is the case with tanned hide, sole leather, and the so-called red-tanned leather, or only after a very continued boiling, as with tawed skins of calves, sheep, or goats. Whatever the differences which obtain in the practical processes for carrying out the conversion, the physical principle involved is the same in all. Knapp's general definition of leather is that it is skin, in which by some means or other the agglutination of the fibres after drying has been prevented.

To a comparatively very recent period tanning was conducted on an empirical basis; it is only by a more accurate knowledge of the histological structure of the skin and of the tannin-containing materials that the real nature of the process has become known; this knowledge being due chiefly to the researches of F. Knapp and Rollet.

That which is converted into leather is, however, not the skin or hide, but really what is known anatomically as the *corium*, that is to say, the inner portion of the skins, from which by mechanical (cutting and scraping) as well as by chemical means (action of lime) the other integuments have been removed. In its most general sense tanning should (1) effect the prevention of putrefaction; (2) render the dry skin a supple, fibrous, tough, non-transparent substance, and not horny as would be the case were the skin simply dried. A well-tanned skin or hide possessing these properties is termed "well finished." The specific process of tanning is of course preceded by some preliminary operations, the aim of which is to "dress" the skins or hides—that is, in scientific terms, to free the corium more or less perfectly from all other integuments. Tanning in the more restricted sense of the word may be effected by a great many organic and inorganic substances; but in practice on the large scale there are employed:—

(1) The tannins of the vegetable kingdom.
(2) Alum and sodium chloride used in tawing or white tanning.
(3) Oils and fats—oil tawing.

Anatomy of Animal Skin.—Leaving the hair out of the question, the skin of the mammalia consists of several layers. The uppermost of these in which the hair is growing, the epidermis, is very thin, semi-transparent, and consists of cells which contain nuclei. This epidermis is covered by a more or less horny layer not possessing any vital properties, which gradually wears off, and is as gradually replaced by the *stratum Malpighii*, or Malpighian net, a structure consisting of cells containing fluid

and nuclei. It is this layer in which the nerves and finer blood vessels are embedded, together with the glands which provide the perspiration. In the tan-yards this layer is known as the *bloom side*, or hair side of the skin or hide. The real corium or derma, situated under the layer just mentioned, does not consist of cells, but is of a fibrous texture, and is that portion of the skin which after tanning constitutes the leather; in the living animal it is separated from the muscles by a more or less strongly developed fat-bearing tissue, the so-called *panniculus adiposus*, which is, however, removed in the dressing, the side of the skin or hide to which it was attached being termed the flesh side. All the histological constituents of skin or hide possess the property of swelling up when put into hot water, and of becoming after more or less protracted boiling converted into glue, more slowly when the skin is taken from old, more rapidly when from young animals. By the action of acetic acid the fibrous tissue of the skin is converted into a jelly-like transparent mass, in which the fibres are not only not destroyed, but are present with their peculiar structure. Alkaline lyes dissolve this tissue but very slowly; while lime- and baryta-water have no other effect on it than simply dissolving therefrom the cellular binding tissue which permeates it, and which is an albumen compound also acted upon by dilute acids.

The various operations of tanning, more particularly the preliminary operations of steeping and dressing, are based upon the behaviour of the different histological elements of the skin and hide with alkaline and acid fluids; but the real process of tanning is based upon the behaviour of the corium with totally different re-agents. This latter substance has the property of combining with tannic acid, several metallic oxides — viz., alumina and the iron and chromium oxides — oxidised fatty matter, the insoluble metallic soaps (compounds of fatty acids—viz., stearic, palmitic, &c.— with lead oxide, &c.), picric acid, pinic acid (present in rosin), and other organic substances, somewhat in the same way as animal and vegetable fibres combine with dyes and pigments. In the most extended sense of the word all these substances are tanning agents, because they possess the property of being precipitated on and in the fibres of the corium, so that when the latter is dried the agglutination of the fibres is prevented, and the natural suppleness and softness of the skin preserved. But in the case of the application of alumina compounds, the softness is only imparted to the tanned skins by the operations of currying and dressing.

Red or Bark Tanning.—This branch of industry concerns itself with the conversion of hides into ordinary leather by the use of tannins.

The tanniferous vegetable matters employed contain as their essential principle tannin which varies in different plants, but which has always an astringent taste and an acid reaction; it gives a black or green coloration with ferric salts, precipitates solutions of glue and of cinchonine, and converts hides into leather. Etti distinguishes quercitannic acid: $C_{17}H_{16}O_9$; the first anhydride or phlobaphen: $C_{34}H_{30}O_{17}$; the second anhydride $C_{34}H_{28}O_{16}$; the third anhydride or Oser's "oak red": $C_{34}H_{26}O_{15}$; and the fourth anhydride or Löwe's oak-red: $C_{34}H_{24}O_{14}$. He considers this tannic acid to be a threefold methylated gallylgallic acid. According to Böttinger the tannin of oak-bark is $C_{19}H_{16}O_{10}$, but that of oak-wood $C_{16}H_{12}O_9$, and the tannin of hemlock-bark $C_{20}H_{18}O_{10}$. Concerning the tannin of nut-galls, it is converted by acids and by fermentation into gallic acid, which is not suitable for the production of leather. Phlobaphen is apparently as important in tanning as tannic acid itself. Every tannin is quickly destroyed by alkaline liquids (lime water, potassa, or ammonia) with access of air, brown humoid products being formed.

Oak Bark.—This substance is for the tanner the most important of all tannin-containing materials, and cannot be replaced by any other. It is the inner bark of several kinds of oak, *Quercus robur*, *Q. pedunculata*, &c., and is stripped from the trees and branches when these have attained an age of from nine to fifteen years, the bark

when cut into splints being termed tan. According to E. Wolff, the quantity of tannin contained in oak-bark is as follows:—

	Tannic acid.	Age of the trees.
In the crude bark covered with the rind	10·86 per cent.	... 41 to 53
„ inside layer of the old bark .	14·43 „	... 41 to 53
„ inside of the bark	13·23 „	... 41 to 53
„ crude bark and inside of bark .	11·69 „	... 41 to 53
„ inside layer and inside of bark .	13·92 „	... 41 to 53
„ inside of bark	13·95 „	... 14 to 15
„ „ „	15·83 „	... 2 to 7

According to Büchner's researches (1867) the quantity of tannic acid contained in the best kinds of oak bark does not exceed 6 or 7 per cent. The fir bark (produce of *Pinus sylvestris*) is one of the best tanning materials, and is frequently used for sole leather; this bark is stripped off the trees immediately after they have been cut down for timber. While J. Feser found from 5 to 15 per cent. of tannin in this bark, Dr. Wagner found only 7·3 per cent. In the United States the bark of the *Abies canadensis* is used; and an extract is in the trade which, according to Nessler's researches (1867), contains 14·3 per cent. of tannic acid. The extract is imported into this country under the erroneous appellation of hemlock extract. The bark of the elm with 3 to 4 per cent. tannin, the bark of the horse-chestnut with about 2 per cent. tannin, and beech tree bark with also about 2 per cent. tannin, are all employed for tanning purposes. The younger branches and twigs of the willow trees yield a bark (3 to 5 per cent. tannin) which is especially suited for certain kinds of glove leather; while another kind of willow bark is used for the tanning of Russia leather.

In Australia the barks of several species of *Acacia* (wattle-barks) are used. The most important species are, *Acacia calamifolia*, *A. pycnantha* and *A. decurrens*. *A. pycantha* may contain upwards of 40 per cent. of tannin.

Sumac.—This substance is, next to oak bark, one of the most important tanning materials; it is the product—the leaves and stems—of a shrub, the so-called tanner's sumac (*Rhus coriaria* and *R. typhina*), which grows wild in Southern Europe and the Levant, and is cultivated in North America and Algeria. The shoots from the roots are collected and planted in June, and after some three years' growth, the shrubs are large enough to admit of the branches and leaves being gathered. The young branches and twigs are cut off, and after drying in the sun, the leaves are beaten off with sticks or clubs and next crushed under mill-stones, sifted, and packed into sacks, and thus sent into the market. The sumac of commerce is a coarse powder, exhibiting a yellow or blue-green colour, and containing 12 to 16·5 per cent. of tannic acid. By keeping, the tannic acid of sumac is converted into secondary products, owing to a spontaneous fermentation. Sumac also contains a yellow dye-stuff which seems to be identical with quercitrin. With sumac should not be confused another material of the same name, but distinguished as Italian or Venetian sumac, and derived from the *Rhus cotinus*, also yielding fustet or yellow dye-wood.* Italian sumac is the pulverised bark of the young twigs and leaves of this plant, which under the name of ruga grows in Southern Europe and also near Vienna; where it is largely used for tanning purposes, being more particularly employed for preparing goat- and sheep-skins.

Dividivi.—The material designated by this name is the seed capsule of some trees found native in Central America, and belonging to the *Cæsalpiniaciæ*; these seed capsules are about 6 centimetres long, are bent as an S, have a brown-red colour, and contain olive-green coloured, egg-shaped, polished seeds. In 1768 the Spaniards brought

* This substance is sometimes erroneously confounded with true fustic, the wood of *Morus tinctoria*.—[EDITOR.]

this material to Europe, where it is used for tanning purposes on account of the tannin contained in the epidermis of the capsules (more correctly *siliquæ*, or pods). The quantity of tannin was found by Müller to be 49 per cent., by Fleck 32·4 per cent., while Dr. Wagner found from 19 to 26·7 per cent. Dividivi is rather an expensive tanning material, but is much used for dyeing purposes. Among the tannin-containing substances which are occasionally imported from abroad may be mentioned the bablah, the produce of the *Acacia bablah* and allied species. This material contains, according to Fleck, 20·5 per cent tannin, while Dr. Wagner found 14·5 per cent. Algarobilla, the seed capsules of the *Prosopis pallida*, a native of Chili, has been also occasionally employed as tanning material in this country. Myrobalans, the fruit of *Terminalia chebula* and of some allied species, are largely imported from Bombay, and are used to a limited extent as a source of tannin, in which they are much richer than is sumac.

Nut Galls.—We understand by this name an excrescence formed on the leaves of the *Quercus infectoria* by the puncture of the female insect of the *Cynips gallæ tinctoriæ*, or oak wasp, effected in the leaves and young twigs in order to deposit its eggs; the juices of the tree collect round the egg, and on hardening form the nut-gall. This material is best collected before the young insect has become fully developed, because then the gall contains the largest quantity of tannic acid. In the market three varieties are met with, termed black, green, and white galls. The black and green variety have been gathered before the insect became fully developed inside the nut; these galls therefore do not exhibit outwardly any hole or opening, but on breaking the gall there will be observed in the centre a small cavity surrounded by a light brown friable substance, which contains the larva of the insect. Galls are generally spherical, but exhibit small irregularities of surface, and are of a black-green or grey colour. The white galls are gathered after the insect is fully developed, and has escaped by perforating the tissue of the gall. This variety is more spongy, and its colour is a red-brown or brown-yellow. Galls of good quality are obtained only from warmer countries, for although galls are formed in our climate upon oak leaves, the quantity of tannin contained amounts to only 3 to 5 per cent. Fehling found in Aleppo galls from 60 to 66 per cent. of tannic acid, while Fleck found 58·71 per cent. of this acid, and 5·9 per cent. gallic acid.

Valonia Nuts.—These are the dried immature acorn cups of two species of oak, *Quercus ægilops* and *Valonia camata*, both being employed in tannin as well as the valonia nuts produced by the puncture of the *Cynips quercus calycis*. The quantity of tannic acid met with in these substances averages from 40 to 45 per cent. In the so-called valonia flour, obtained by grinding the acorns belonging to this class, Dr. Wagner found from 19 to 27 per cent. of tannin. The acorn cups are imported under the name of *drillot*, and according to Rothe these contain from 43 to 45 per cent. of tannin.

Chinese Galls.—Under this name has been known in the trade since 1847, and imported from Japan, China, and Nepaul, the excrescence upon a kind of sumac, *Rhus javanica* and *R. semialata*, produced by the puncture of the *Aphis sinensis*. This gall-nut is rather oblong or bean-shaped, with an irregular surface covered with a yellow-grey felt; the length varies from 3 to 10 centimetres, and the thickness from 1·5 to 4 centimetres; the texture is horny; the quantity of tannin varies from 60 to 70 per cent.

Cutch.—The substances long known in medicine under the name of catechu and kino have been for the last fifty years also employed as tannin materials. They are vegetable extracts, that known as cutch (trade term) being obtained by exhausting with boiling water the pith of the wood of the *Acacia catechu*, a tree met with in different parts of the tropical regions of Asia. The liquor obtained by boiling the pith-wood in water is inspissated, and on cooling forms a solid mass, which is brought

into commerce in various shapes and named after the port of shipment. Bombay cutch is met with in the shape of large square blocks, through and round which the leaves of a kind of palm-tree are placed. The colour of the fracture of this substance is a brown-black with a fatty gloss; externally the mass is dull and friable. Bengal cutch is prepared from the nuts of the *Areca catechu*, and occurs in commerce as large, irregularly shaped cakes, externally brown, internally more yellow-coloured. Gambir is a variety of cutch prepared in Sumatra, Singapore, and Malacca, and especially in the Island of Riouw, from the leaves and stems of the *Uncaria gambir*. The dry extract occurs in commerce in small cubical blocks, which are light, of a cinnamon-colour, and very friable, the fracture being earthy. All these substances contain about 40 to 50 per cent. of a peculiar kind of tannic acid or catechu-tannic acid, the formula of which, according to J. Löwe, is $C_{15}H_{14}O_6$, as well as a peculiar acid, catechueic acid, $C_{16}H_{14}O_6$, not of much use in the tanning process.

Kino.—This drug is very similar to catechu, and is said to be the extract prepared from various plants—viz.:

African kino from	*Pterocarpus erinaceus.*
East Indian kino from	*Pterocarpus marsupium.*
East Indian kino, according to others, from	*Butea frondosa.*
West Indian kino from	*Coccolaba uvifera.*
Australian kino from	*Eucalyptus resinifera.*

Kino is met with in small, angular, brittle, brown-red to black-coloured masses, the powder of which is always brown-red. It is soluble in hot water and alcohol, yielding a blood-red solution of an astringent and sweet taste. Kino contains from 30 to 40 per cent. of a tannic acid similar to that contained in cutch; both of these materials are especially useful in so-called quick tanning.

Estimation of the Value of the Tanning Materials.—The value of all the tanning materials entirely depends upon the quantity of tannic acid they contain. The latter is soluble in water, and more or less completely precipitated from that solution by various re-agents, such as glue and animal skin, copper acetate, iron acetate, cinchonine and quinine, while a solution of potassium permanganate completely destroys the tannic acid. Upon these properties the following properties have been based for the approximative estimation of the quantity of tannic acid present in various tanning materials:—

1. Precipitation by glue or skin:—
 (*a*) Weighing of the skin before and after immersion in the liquor containing tannin, the increase of weight giving the quantity of tannic acid (DAVY).
 (*b*) Precipitation with gelatine solution of known strength (FEHLING).
 (*c*) Titration by means of aluminated solution of glue (G. MÜLLER).
 (*d*) First discover the specific gravity of the tannin solution by means of an areometer, next remove the tannin by skin, and then again take specific gravity of liquid, the decrease being proportionate to the quantity of tannin in the original liquor (C. HAMMER).
2. Precipitation of tannin by copper acetate, and estimation of the relation between tannin and copper oxide in the precipitate:—
 (*a*) Volumetrically (H. FLECK); or
 (*b*) By the gravimetrical method (E. WOLFF).
3. Volumetrical estimation of tannin by iron acetate (R. HANDTKE).
4. Oxidation of tannic acid by potassium permanganate (LÖWENTHAL).
5. Precipitation of tannin by means of cinchonin, the solution of which is tinged red by means of magenta. 1 gramme of quercitannic acid requires 0·7315 gramme cinchonine, equal to 4·523 grammes of crystallised neutral sulphate of cinchonin (R. WAGNER).

The subjoined table shows the composition of several tanning wares:—

	Total Organic Extract.	Non-tanning Matters.	Tanning Matters.	Tanning Matters calculated as Tannin.	Proportion of Tannin to total Tanning Matters.
Dark pine bark, Carinthia . .	22·34	12·19	10·15	5·23	0·5152
„ „ Thuringen . .	30·56	14·30	16·26	10·24	0·6298
Light Swiss do.	31·58	14·82	16·76	11·89	0·7094
Nearly white pine bark from Bohemia	26·72	14·74	10·98	8·31	0·7586
Oak bark, Rhine	17·02	6·43	10·59	7·46	0·7044
„ Hungary . . .	17·12	8·66	8·46	6·05	0·7151
„ Sweden . . .	22·08	10·30	11·78	8·74	0·7420
„ Saarlohe . . .	23·32	10·12	13·20	9·97	0·7553
Quebracho wood (red) . .	22·46	1·90	20·48	18·30	0·8935
„ „ (white) . .	27·32	2·44	24·88	21·03	0·8452
Valonias	38·40	10·00	28·40	28·81	1·0144
„	37·28	10·84	26·44	26·87	1·0162
Sumac	41·20	23·92	17·28	16·89	0·9774
„	25·15	17·80	7·35	6·90	0·9388

The Hides.—The skins of almost all quadrupeds might be converted into leather by tanning; but the tanner chiefly prepares his leather from the hides of cattle, occasionally from those of horses and asses, as well as of pigs. The quality of the hides not only depends upon the kind of animal, but also upon its fodder and mode of living. The hides of wild cattle yield a more compact and stronger leather than those of our domesticated beasts; among these the stall-fed have better hides than the meadow-fed or grazing cattle. The thickness of the hide varies considerably on different parts of the body, the thickest part being near the head and the middle of the back, while at the belly the hide is thinnest. These differences are less conspicuous in sheep, goats, and calves. As regards sheep, it would appear that their skin is generally thinnest where their wool is longest.

The hides of bulls and oxen yield the best and stoutest leather for soles. In the raw—untanned—state, and with the hair still on, the hides are termed "green" or "fresh." Fresh or green hides are supplied to the tanners by the butchers, or are imported either dry or salted. A hide weighing in the fresh state from 25 to 30 kilos. loses by drying more than half its weight. South America (Bahia, Buenos Ayres, &c.) exports a large quantity of hides, both dry as well as salted, and cured by smoking. The hides of cows yield generally an inferior grained leather; but South American cow hides may be worked for light sole leather. Calves' hides, again, are thinner, but when well tanned, curried, and dressed, yield a very soft and supple upper leather for boots and shoes. Horse hides are only tanned for saddlery purposes, while sheep- and goat-skins and the skins of lambs are tanned—or more generally tawed—for the purpose of making wash-leather, morocco, glove-leather, bookbinders' leather. Pigs' hides and seals' skins are tanned for saddlery purposes.*

The Several Operations.—The several operations of the oak bark tanning process may be reduced to three, viz.:—A. The cleansing and dressing of the hide on the hair and flesh side; in other terms, the separation of the corium from the other integuments. B. The true tanning. C. The currying and dressing operation, by which the tanned hide becomes a saleable article. These three operations are again subdivided as follows:—

A. The cleansing of the hide:—

(1) Steeping and macerating the hide.
(2) Dressing the flesh side.
(3) Dressing the hair side.
(4) The swelling of the cleansed hide.

* The hide of the porpoise yields an excellent leather for stout boots.—[EDITOR.]

B. The tanning of the cleansed hide, performed either by placing it in tanks or pits with oak bark and water, or in a liquor of these previously prepared, or by the so-called quick method.

C. The dressing and currying of the tanned hides, by which is understood all the operations which tend to improve the compactness of texture, or give a better grain and better appearance to the leather, together with softness, toughness, suppleness, and colour.

A. *Cleansing the Hides.*—This operation includes:—(1) The steeping or macerating of the hide in water for the purpose of rendering the texture uniformly soft and so supple that it may be bent without danger of cracking, while, on the other hand, steeping also effects a cleansing of the hide by removing from it blood and dirt. The fresh hides of recently slaughtered animals require a maceration in water for some two or three days, but dried, cured, or salted hides have to be left macerating for some eight to ten days. This operation should, if possible, be carried on in a stream of water; but if there is no such convenience, then the hides are placed in large tanks; in either case the hides are taken out twice daily and put back into the water again. When the hides have become quite soft, they are—(2) cleansed or dressed on the flesh side by being placed with the hair side downwards on a "tree," a stout semi-circular plank, one end of which is placed on the ground while the other is supported by a trestle, so that the plank is in a sloping position. The workman has a so-called dressing-knife, a tool to which handles are fastened, and which is bent so as to form a slight curve; with this knife he shaves, or, as it were, planes off, from the hide all fatty tissue and integuments which are situated between the hide and the muscles. At the same time the water is squeezed out of the hide to some extent. After a preliminary or first dressing, the hides are again placed for twenty-four hours in water; the dressing and planing is then quite finished, and the hides having been well washed, are left to drain on the tree ready for removing the hair. In some instances the hides are washed by the aid of "possing-sticks," and "fulled" by means of machinery, by which the operation is greatly shortened, so much so, that two to three days suffice, instead of, as is usual by the aid of manual labour, eight to ten days. (3) This operation aims at the removal from the corium of the epidermis and hair-containing integuments. As the hair and integuments connected therewith are very firmly attached to the corium, the removal can only be safely proceeded with, so as to leave the corium uninjured, by the employment of a menstruum, which more or less dissolves and causes the epidermis to swell up. For this purpose the hides are usually placed in lime-pits, the effect of the lime being the partial dissociation (in an anatomical sense) of the epidermis, so that it and the hairs may be readily removed by mechanical means.

The effect is usually obtained by—(*a*) Sweating; (*b*) Liming; (*c*) Application of rusma or compounds of calcium sulphide.

(*a*) A semi-putrefactive fermentation called sweating is employed in the case of thick hides, such as serve for sole leather, which are not placed in lime owing to the fact that it cannot be completely removed, and would render the leather brittle. The operation of sweating consists in placing the hides one upon the other, the flesh side turned inward, some salt or crude wood vinegar having been first rubbed in, in a tank, or box, which can be closed, so that the heat generated by the fermentation which sets in may be confined as much as possible to aid the action. As soon as the evolution of ammonia is perceptible, the hides are ready for the removal of the hair, which is shaved off, together with the epidermis, by the aid of the dressing-knife. Instead of causing the sweating to be done by fermentation, the hides are sometimes hung on laths in rooms either heated by means of steam or by fire. A temperature of from 30° to 50° should be kept up, together with a good current of steam, by which the epidermis is thoroughly softened. In order to prevent any injury to the corium, the hides are

sometimes submitted to what may be termed a cold sweating process, consisting essentially in placing the hides in water-tight tanks, in which there is a constant current of fresh water, the temperature being kept at from 6° to 12°. The hides thus submitted to a constantly moist atmosphere become, after from six to twelve days, without any perceptible putrefaction, fitted for the removal of the epidermis and hair.

(*b*) The liming of the hides not only prepares them for the removal of the hair, but also saponifies the fatty matter; and though the lime soap thus formed is insoluble in water, it is removed by subsequent mechanical and chemical operations. The operation of liming is carried on in pits, into which, along with milk of lime, the hides are placed so as to be quite covered. Usually several (three to five) pits are in use at once, each of which contains a different quantity of lime. That the milk of lime should be frequently stirred in these pits is of course evident. The hides remain in the lime-pits for from three to four weeks.

(*c*) The very thin skins of the smaller animals will neither sustain sweating nor liming, and are therefore treated with ruṣma, a salve-like mixture of orpiment 1 part, with 2 to 3 parts slaked lime. By the rubbing in of this mixture on the hair side of the skins, the hairs are so softened as to make their removal an easy matter. Böttger states that calcium hydrosulphuret has the same effect; hence the lime of the purifiers of the gas-works have been of late years frequently employed for treating hides as well as skins, with the additional advantage of yielding a better leather.

Stripping off the Hair.—As soon as the hides are sufficiently prepared to admit of the removal of the hair and epidermis, they are stretched out on the tree and the integuments peeled off by the aid of the blunt dressing-knife. In order to give to the dressing-knife a better grip, the workman strews some fine sand on the hide, and if he has to deal with very heavy and thick hides, uses a large and rather sharp knife. When the hair and the epidermis have been removed, the hides are again washed and macerated in water, and after this dressed; that is to say, reduced as much as possible to an equal thickness, while the waste—tail, leg, and head-pieces—are cut off, and the hide planed, thereby losing some 10 to 12 per cent. in weight.

Swelling the Hides.—The aim of this operation is to remove the lime, and also to render the corium more capable of readily absorbing the tan materials. This end is attained by placing the hides in a so-called sour bath, made of refuse malt and bran, which by acid fermentation yields as active principles propionic, lactic, and butyric acids.

The lime is removed from the dressed hides when placed in this acid liquid, and the lime-soap present becoming decomposed, the fatty acids set free float on the surface of the liquid. The soluble lime salts are completely removed from the hides by a subsequent thorough washing with water. The thickness of the hides is doubled by the swelling action of the acid liquid, aided by the mechanical action of the carbonic acid evolved from the calcium carbonate deposited within the fibres of the hides; while the butyric acid fermentation distends the fibres of the hides by the gases thereby evolved. When the hides have not been treated with lime but have been submitted to a "sweating," they do not require the acid bath, but are simply placed in water for the purpose of swelling them. Yet the sour bath is preferable owing to its more regular action.

Instead of using the preceding mixture for the purpose of removing the lime and of swelling the hides, they are often placed in acid tan-liquor (red tan liquor)—that is to say, a liquor containing exhausted oak bark solution which has served for tanning. This liquor appears to contain also large quantities of lactic and butyric acids. The dressed hides are first placed in a diluted red liquor, and then in a stronger liquor, this operation taking some twelve to fourteen days. Macbride and Seguin have proposed to substitute very dilute sulphuric acid (1 in 1500), but although

by the use of this acid the operation of swelling is rendered far more rapid, the quality of the leather is impaired. Phosphates and animal excreta which contain a large quantity of uric acid, such as that of dogs and of pigeons, have been, and in many cases are still, used for the purpose of swelling hides, especially skins of sheep, calves, and goats.

B. *The Tanning.*—The main object of the operations just described is first to obtain the corium as much as possible separated from the other integuments and textures belonging to the skin, and next to render the corium as much as possible permeable by the liquor in which the vegetable matter containing tannin is dissolved. In practice it is taken for granted that a dry hide gains one-third in weight by being converted into leather, consequently it absorbs that proportion of tannin.

The impregnation of the fibres of the hide or skin with tannin is effected by two different methods, viz.:—

(1) By placing the hides between layers of oak bark chips in a tank, so-called tanning in the bark; or

(2) By immersing the hides, first in a dilute, and then in a concentrated aqueous infusion of oak bark.

(1) *Tanning in Bark.*—This mode of tanning is at the present time confined to heavy hides intended for sole leather. The tanks in which this operation is carried on are made of wood, either oak or fir, are of course watertight, and are usually sunk into the soil. Brick cisterns lined with cement are occasionally used, but are objectionable, at least when newly built, on account of the deteriorating action of the lime and cement upon the oak bark. In some parts of Germany tanks constructed of slabs of slate or sandstone are used. Each tank has sufficient capacity to contain from 50 to 60 hides. On the bottom of the tank is first placed a layer of exhausted (spent) tan, and upon this a layer of some 3 centimetres in thickness of fresh bark, then a hide with the hair side downwards, again a fresh layer of oak bark, and again a hide, alternately until the tank is nearly filled, care being taken to put some more bark on the thickest part of the hides, and to fill not only all interstices with bark, but to put on the top a layer of some 30 centimetres thickness of spent tan. Water is next poured into the tank until it stands a few centimetres above the topmost hide; this having been done, a lid—in England loose planks—is placed on the tank, the contents of which are left undisturbed for some time. When Valonia flour is employed with the oak bark only half the quantity of the latter is necessary.

The hides are left in "the first bark" for from eight to ten weeks, the period being a little shortened if Valonia flour is also used. Before all the tannin has been absorbed, and as a consequence the formation of volatile and odorous acids (valerianic, butyric, &c.) has commenced, the hides are transferred to another tank, and again placed between alternate layers of fresh bark, the only difference in the arrangement being that the hides which were first placed on the top are now laid at the bottom of the tank. The hides are now left for three or four months, so as to thoroughly absorb the tannin. They are next placed for some four or five months in another tank which contains less bark. In the case of very heavy and thick hides the process is repeated four or five and even six times. The quantity of bark required for obtaining thoroughly well-tanned leather depends partly on the quality of the bark and somewhat on the condition of the hides. Usually the tanners reckon that the quantity of bark required amounts to from four to six times the weight of the dry hides; and taking the weight of these at an average of 20 kilos there will be required :—

For the first tank		40 kilos.	of bark
,,	second	35	,,
,,	third	30	,,
		105	,,

A dried and well-tanned hide weighs about 22 kilos., or from 10 to 12 per cent. more than the dry raw hide. A thoroughly tanned hide exhibits, when cut with a sharp knife, a uniform texture, free from fleshy or horny portions, while the grain on the hair side should not, on being bent, slowly exhibit signs of cracking.

(2) *Tanning in Liquor.*—The thinner hides, and indeed most skins (when tanned, as distinguished from tawing), are placed in infusions of the tannin-containing material. There are various methods in use for this operation, which is based mainly upon a thorough uniform swelling of the hides, so that when these are placed in weak liquors the tannin may penetrate readily and uniformly. The hides are, in fact, very gradually tanned. When taken from the liquor the fluid is forced by mechanical means out of the hides before they are placed in a stronger liquor, which is obtained by exhausting the tanning materials by the aid of cold water. The thinner kinds of hides are thoroughly tanned in from seven to eight, the heavier hides in from eleven to thirteen weeks.

Quick Tanning.—Many methods—some quite impracticable, and most of them thoroughly irrational—have been proposed for converting hides into leather in a very short time. Of these different methods we briefly mention the following :—(1) The hide is simply placed in an infusion of the tannin-containing material—Macbride's process, improved by Seguin (1792). Application of hydrostatic pressure to force the liquor through the hides, kept from contact with each other by a stout woollen tissue. (2) Circulation of the fluid containing tannin, several tanks being connected together by means of pipes, and the liquor being forced through the tanks by means of pumps (Ogereau, Sterlingue, and Turnbull's methods). (3) The hides are sewn together so as to form sacks, which are filled with oak bark chips and water, and then placed in an aqueous solution of cutch, to which, in order to increase its specific gravity, coarse molasses is added—Turnbull's method by increased endosmose. At the time this mode of proceeding was brought forward, the diffusion of liquids by dialysis (discovered by Graham in 1861) was unknown. (4) Motion of the hides in the tannin-containing liquids, the hides being placed in a cylinder constructed of wooden laths, so as to leave open spaces between them. This cylinder is immersed horizontally in the liquid to a greater or less depth, so that in every revolution the hides are alternately in and out of the liquid—Brown, Squire, and C. Knoderer's methods. (5) Application of mechanical pressure to the hides, which having been from time to time removed from the tanning tanks, are placed upon perforated planks, and either pressed under a heavy roller or are placed in a press—Jones, Nossiter, Cox, and Herapath's method. (6) Application of hydrostatic pressure for the purpose of causing the tan-liquor to penetrate the hides, which are sewn together so as to form bags, which, having been filled with oak bark liquor, are placed in suitably constructed vessels, so that hydraulic pressure may be applied without fear of bursting the bags; or the hides are fastened by means of screws and bolts, placed on a framework which is immersed in a well-constructed cistern filled with tan-liquor, hydraulic pressure being applied—Drake, Chaplin, and Sautelet's methods. (7) Snyder's method of punctation, consisting in perforating the hide over its whole surface, the punctation being effected by sharp needles, so as to constitute artificial pores. The experiments of Knapp have proved the thorough irrationality of this plan, it having been found that the hide is so permeable to tannin-liquor that a piece of calf-skin, when placed in a solution of tannin of the consistency of syrup, is thoroughly well tanned in about an hour's time. (8) Application of a vacuum by placing the hides in a vessel from which the air may be withdrawn by the aid of air-pumps; tan liquor having been forced into the vessel, the air is re-admitted and again withdrawn—Knowly and Knewsbury's plan. Knoderer has recently found that by a judicious combination of the vacuum method, followed by motion and fulling of the hides in the tan-liquor, the operation of tanning is much

shortened. The reader should bear in mind that the methods here alluded to are not now in general use.

Dressing or Currying the Leather.—When the hides have been converted into leather by the processes described, they are not by any means fit for use nor ready for sale as a finished material, but require to be dressed, or, as it technically termed, curried, an operation not necessarily performed by the tanner—at least, not in England and France. The several operations are not similar for all kinds of leather, but depend to some extent upon the use to which it is intended to be put. For instance, sole leather is submitted simply to a process the object of which is to render it sufficiently stiff and compact, so as not to alter its shape by wear.

Sole Leather.—The dressing or currying of this kind of leather consists mainly in submitting it to a mechanical operation of hammering, by which the material is rendered more compact. As soon, therefore, as the hides are taken from the tanning tanks, the adhering spent tan is brushed off with a broom, after which the hide is dried in a cool place, and when dry is laid flat upon a polished stone slab, and then beaten with wooden or iron hammers, an operation in large establishments performed by hammers moved by machinery.

Upper Leather.—The dressing of this kind of leather, chiefly used by saddlers and boot and shoe makers, is a far more complicated process, and depends in a great measure on the use for which the leather is intended.

The Paring.—The first of these operations is the paring or whitening, which means the cutting away, by the aid of a tanner's shaving-knife, of all portions of the hide which are too thick, so that the whole hide may be made of uniform thickness. This operation is carried on upon the tanner's "wooden leg," the hide being placed with the hair-side downwards. When goat, lamb, sheep, or calf-skins are to be pared, they are placed upon a polished slab of marble, and, having been well-stretched, the raw or projecting parts are cut off with the tanner's shaving-knife.

The Scraping or Smoothing.—The aim of this operation is similar to that of the former, and more particularly is employed in the case of leather intended for making gloves. The leather is first dried and next fixed on the "perching-stick," one end of the skin remaining free, the other being taken hold of by the operator with a pair of forceps. The skin having been stretched, the perching-knife, a highly polished somewhat convex steel disc of from 18 to 30 centimetres diameter, and provided in the centre with an opening fitted with a piece of leather serving as a handle, is brought into use, the portions of the skin which require to be pared off being usually indicated by being rubbed over with chalk.

Graining the Leather.—As in consequence of the drying of the leather the grain has become flat, smooth, and unequal, it is raised by an operation performed by means of the pommel, also termed the graining- or crimping-board, a piece of hard wood 30 centimetres in length by 10 to 12 centimetres breadth, flat and smooth on the top, but on the opposite side, in the direction of the length, somewhat curved, so that it is thickest in the middle, this part being provided with parallel notches, which are occasionally sharpened by means of a file; a leather strap is fastened to the top as a handle. The leather to be grained, having been placed on the dressing-table, is fastened to the edge of the wooden board by means of iron clamps, and those portions of the leather, the grain of which has to be raised, having been somewhat bent, are rubbed with the pommel so as to render the grain uniformly visible.

Polishing with Pumice-Stone.—Such kinds of leather as require no grain (for instance, the leather used in carding machines) after having been pared, are moistened and then rubbed over on both sides with pumice-stone, being thus rendered smooth.

Raising the Grain Slightly with Pommels of Cork.—Leathers which require a higher

gloss, such as the coloured leathers, are treated with a pommel made of cork, by which they are made to assume a velvety appearance.

Smoothing with the Tawer's Softening Iron.—If a still higher gloss is required, the leather is first smoothed, or rather ironed, with iron or copper "sleekers," and next polished with glass sleekers, a stout cylindrical piece of glass, 0·3 metre in length by 10 centimetres diameter, the leather being placed on a tanner's wooden-leg.

Rolling.—Leather intended for saddles, in order to impart to it the appearance natural to hog's leather, is passed through rollers, the surfaces of which are provided with blunt points, which, being forced into the leather, give to it the desired appearance.

Finishing Off.—In order to remove from the leather any creases and other inequalities of surface, it is damped, and then smoothed with a flattening-iron, or, if the skins are thin, with a piece of horn provided with blunt teeth.

Greasing.—When the upper leather is required to be very supple and soft, it is greased; that is to say, it is rubbed with a mixture of fish-oil and tallow, or better, with the peculiarly modified fish-oil which has been used in "chamoising," having been recovered by the aid of a solution of potash from the chamois leather skins. The hides to be greased are first moistened, and having been rubbed with the greasy matter, are dried in heated rooms, so that the hides, by actually combining with the fatty matters, become, as it were, tanned and tawed at the same time. The greasing is therefore not simply an operation of dressing, but in reality a second tanning (technically tawing) process.

The black colour usually seen on the surface of leather required for saddlery and boot-making is imparted to the hides by rubbing them with a fresh solution of oak bark and then sponging them over with a solution of copperas to which some blue vitriol has been added; the hides are then again dressed, and lastly rubbed with a paste made of fish-oil, tallow, lamp-black, yellow wax, soap, and copperas, the object of this operation being to protect the leather from the injurious effects of the shoe-blacking, which usually contains sulphuric acid.* Finally, the leather is painted or brushed over with a mixed tallow and glue solution, and then, having been polished again with glass, is ready for sale. In order to keep leather supple and soft, it is best to rub it with a mixture of fish-oil and lard.

Yufts, Jufts, or Jufti, Russia Leather.—Under the name of yufts is understood a peculiar kind of leather, usually of a red or black colour, which is very water-tight and strong. This kind of leather was formerly made exclusively in Russia, whence it was obtained in large quantity, the name being derived from the Russian *Jufti*, signifying a pair, and apparently due to the fact that, in tanning, the hides are sewed together in pairs. The hides usually prepared for Russia leather are those of young cattle; sometimes, however, the hides of horses and the skins of sheep, goats, and calves are employed. The operations for preparing yufts are:—(1) The cleansing of the hides, performed in the usual manner with lime. (2) The swelling of the hides in an acid bath prepared with malt, exhausted tan-liquor, or with kaschka (excreta of dogs rubbed up with water). (3) The tanning, not performed with oak bark, but with the barks of various kinds of willows, fir and birch bark being also used. The dressed hides are first placed for some days in partly exhausted bark, and are then put into the tanning tanks along with bark (as above described), or are sometimes placed in a warm infusion of the tannin-containing materials. The tanning continues for five or six weeks. (4) The tanned hides are placed on the planing-block for the purpose of draining, and are next impregnated with *diggut* or *elachert*, oil of birch, obtained by a process of dry distillation from birch wood. This oil contains creosote, phenol (of a peculiar kind according to Louginine), and paraffine. It is rubbed into the hides on the flesh side, and

* For a shoe-blacking without acid see *Chemical News*, vol. xxiv. p. 120.

when thoroughly impregnated they are stretched until they become soft and supple. The hides are next rubbed on the hair side with a solution of alum, and then grained and dried. The dry hides are dyed in pairs, sewn together so as to form a sack, into which a decoction of dye material is poured. When a red colour is desired, the dye is prepared from sandal-wood and Pernambuco-wood extracted with lime-water, to which some potash or soda is added. In more recent methods the hides are dyed by being brushed over five or six times with the dye material. The dry leather is finally dressed by the mechanical operations previously described. The use of yufts for bookbinding and other purposes is well known. Owing to the empyreumatic oil with which this kind of leather is impregnated insects do not attack it.

Morocco Leather.—By morocco leather is understood a kind of leather which, when genuine, is obtained from goat- or kid-skins, and is very soft, elastic, highly coloured, and not lacquered. We distinguish between *genuine* morocco and the imitation obtained by the splitting of calf, sheep, and other skins, as chiefly employed in bookbinding.

The preparing of morocco leather is undoubtedly one of the many industrial discoveries of the Saracens; even at the present day a great deal of morocco leather is made by their descendants in Northern Africa and the Levant. The preparation of good morocco leather requires very great care, especially as regards the preliminary operations. The skins are deprived of the hair by the aid of lime and sweating. The tanning material in general use is sumac, the skins being sewn up so as to form sacks into which water is poured together with pulverised sumac; by this mode of employing the tanning matter the operation is finished in three days. Calf and sheep skin are very generally tanned in England by the same method. The dyeing of morocco leather is not performed in the Oriental countries; the dry tanned skins are exported under the name of Meschin leather (*cuir en croutes*) to be dyed and dressed in Europe.

Dressing Morocco Leather.—The skins are dyed and next dressed. The dyeing is performed—(*a*) by means of the dye-vat (for genuine morocco), or (*β*) with the brush (for imitation morocco). (*a*) The operation of dyeing with the vat is performed in a small trough large enough to hold one skin, and filled with dye-liquor at 60° from a larger tank. The workman pours in no more of the dye material than can be conveniently absorbed by the skin, which is continually moved to and fro. The dyed skins are layed out flat, and from two to four dozen placed one upon the other. The dyeing operation is repeated several (three to five) times, care being taken to turn the heap over so that the undermost skin is placed on the top of the heap previous to beginning the dyeing operation again. The dyed skins are washed in water and next dressed. (*β*) The imitation morocco is dyed by the dye-liquor being uniformly brushed over the skins; these having been first stretched on a table, the dye-liquor is brushed over more than once so as to produce a uniform hue. The effect of the dyeing is greatly enhanced by the dressing of the skins and the fine grain given to them. The dyed skins are first rubbed on the hair-side with linseed oil applied by means of a piece of flannel. The calendering or glazing by machinery is the next operation, after which the peculiar appearance of the surface is imparted by means of strong pressure or so-called platting. Yellow skins are not glazed, because their colour would thereby become a brown. The aniline colours are now largely employed in dyeing skins.

Cordwain, Cordovan Leather.—This differs from morocco only by being prepared from heavy skins, and by retaining its natural grain or not being platted. It is usually met with dyed red, yellow, or black.

Lacquered Leather.—This kind of leather, now largely used by coachbuilders and for making shoes, boots, helmets and other military accoutrements, is an invention of

the present time, its great merit being its property of resisting water, and in being supple and soft, while the lacquer, if well laid on, should not crack nor peel off. Only black lacquered leather is generally met with. On the tanned, rarely tawed, hide, which has not been greased, is very uniformly laid a varnish, which is thick and tough while cold, but thinly fluid when warm; this having been done, the hide is placed in a brick-built stove kept at 50°, where the varnish dries after having become so fluid as to run uniformly over the surface of the leather, which is placed quite horizontally. The coloured lacquers are generally more thinly fluid and are dried at a lower temperature. The hides chiefly used for lacquering are cow-hides; or a thin hide is obtained by splitting thick hides and lacquering them.

The leather in use by pianoforte-makers for covering the hammers is prepared by a process usually kept a trade secret. This kind of leather requires to be soft and very elastic. All that is known about the process of preparing this material is that it is obtained by tanning and tawing (chamoising) combined; the hair having been removed, but not the epidermis, the hide is first fulled in oil, then washed in lye, bleached in the sun, and next tanned in a tepid oak bark infusion. Danish leather is prepared by tanning sheep-, goat-, kid-, and lamb-skins with willow bark; such leather being chiefly used for gloves. It is distinguished by its strength, suppleness, and bright colour.

Alum Tanning—Tawing. — Alum-tanning makes use especially of aluminous salts for converting hides into a white or light-coloured leather. It has three varieties:

(1) Ordinary tawing, in which thin hides, such as those of sheep and goats, are worked up with a mixture of alum and common salt without the use of oil.

(2) Hungarian tawing, in which the hides of oxen, buffaloes, horses, &c., are worked up without a previous treatment with lime and then saturated with oil. Closely connected with this process is the preparation of Klemm's fat-leather.

(3) French or Erlangen tawing, for obtaining glove-leather from the skins of kids, young calves, lambs, rarely of chamois.

(4) Preparation of leather with insoluble soaps and its tanning with compounds of iron or of chrome (Knapp's Leather).

(1) *Common Tawing.*—The tawer obtains sheep-skin, or occasionally goat-skin, either with the wool off or "in the wool," as the term runs, in the latter case greater care being required, because the value of the wool, which, by careful working may be obtained in good condition, refunds a considerable portion of the expense of the operation by its sale. The various operations of tawing are in a certain measure similar to those of tanning.

The steeping and planing is carried on as in the tanning process. The workman places ten skins on the planing-tree, and dresses each skin with the dressing-knife on the hair as well as on the flesh side; next, the wool or hair is shaved off after the skins have been first treated with the lime; but when "in the wool" the skins are cleansed with thin lime-water, which is laid on the flesh side of the skin by a brush made of cow's hair, so that the wool is not brought into contact with lime. The wool is removed, not by a planing-iron, but by means of a piece of wood somewhat sharpened. The wool having been removed, the skins are brushed over with a mixture of equal parts of lime and sifted ashes; next the head and leg strips of the skin are turned inside. Each skin is then folded together and beaten, in order to prevent the wool being touched by the lime. The skins are left in this condition for eight to ten days until the wool is loosened. The skins are next thoroughly washed on the flesh side as well as on the wool side in order to remove the lime and dirt; this having been done the wool is partly pulled off by the hands, partly removed by a blunt tool. The skins thus deprived of wool are placed in the lime-pit and further treated as just described. In order to remove the paste adhering to the skins they are, on being removed, placed

in a tank, where, owing to the quantity of animal matter dissolved in the water, a fermentation has arisen accompanied by an evolution of ammonia. By the action of this alkali a large portion of the fatty matter contained in the skins is removed. After being taken from the lime-pit the skins are placed on the dresser's block, and some parts, such as the ears, skin of tail, portion of top part of chest, are cut off and thrown aside for the glue-boiler. The skins are put over-night to soak in water, and then again placed on the dressing-block in order to be planed with a blunt iron on both sides of the skin; this operation is repeated after the skins have been placed in a tank containing water, and while there thoroughly beaten with a heavy wooden "possing-stick" in order to remove lime. In the subsequent planing the lime and lime-soap are forced out, and any wool that has remained shaved off. In order to dissolve the last traces of lime the skins are placed in an acid-tank containing bran and water, in which by fermentation lactic and acetic acid have been formed. These acids convert the lime of the skins into soluble salts, while the process causes the swelling of the skins, which thus become better adapted to absorb the tanning material. The skins remain in the sour-tank for two to three days. The tanning material consists for 1 dicker (10 skins), of an alum lye, containing 0·75 kilo. of alum, and 0·30 kilo. of common salt dissolved in 22·5 litres of boiling water. 1 litre of this liquid is poured into a trough, and having become tepid, each skin is separately thoroughly washed with and soaked in it, and then put aside without being wrung out, the skins being placed one upon the other so as to form a heap. After lying thus for two or three days, the skins are wrung out and hung up to dry slowly by exposure to air.

As regards the theory of the action of the alum lye in the tawing operation, it was formerly believed that only the aluminium chloride—formed by double decomposition between the constituents of the common salt and the aluminium sulphate of the alum (the alkaline sulphates being considered useless)—was active, and that a basic aluminium chloride (aluminium oxychloride) combined with the skin, there being left in solution aluminium chloride. It was also known that aluminium acetate, if used instead of alum lye, was quite as active and yielded excellent results. The experiments made by Dr. Knapp, sen., with alum, aluminium acetate, and aluminium chloride have proved that no decomposition ensues when the aluminium salt is taken up by the skin, the quantity taken up being for the undermentioned salts as follows:—

Of alum	8·5 per cent.
Of aluminium sulphate	27·9 „
Of aluminium chloride	27·3 „
Of aluminium acetate	23·3 „

The aluminium salts do not, however, combine with skin under all conditions in the same quantity as just mentioned, as experience proves that the skins absorb more when placed in concentrated than when in dilute solutions. As regards the part played by the common salt in the preparation of the alum lye, the salt is not there simply to bring about the conversion of the aluminium sulphate into aluminium chloride (recent experiments made by Knapp in 1866 have proved that by employing 1 mol. of potash alum and 3 mols. of common salt, = 37 per cent., no mutual decomposition ensues), but the salt is in this process active by itself, partly aiding dialytically the action of the alum, partly owing to its property—possessed also by alcohol—of withdrawing from animal tissues the water they contain sufficiently to prevent the fibres from becoming glued together by the drying of the substance, thus promoting the formation of leather. The dry and tawed skins will be found to have become shrunken and stiff, having lost much of their suppleness and flexibility. In order to remedy these defects the skins previously damped with water are submitted to a mechanical operation, being placed on the convex side of a curved iron, and stretched by being drawn between this fixed iron and a movable steel plate, which is fitted closely upon the other. After having

been thus softened, the skins are stretched on a frame for some time to become dry. When dry they are ready for sale, the leather thus obtained being largely used under the name of white skins for the lining of boots and shoes.

(2) *Hungarian Tawing Process.*—This process is distinguished from that just described, inasmuch as the heavy hides of oxen, buffaloes, cows, horses, &c., are made into leather for saddlery and other purposes, while sometimes also the skins of wild boars and of other animals are thus tawed for making flail strings. The raw hides are first soaked in water to remove blood and impurities. Next the hair is shaved off by means of a sharp knife. This operation performed, the hides are put into an alum lye, which for a hide weighing 25 kilos., consists of 3 kilos. of alum, 3 of common salt, and 20 litres of hot water. This liquor when tepid is poured into an elliptical tub in which the hide is placed.

One of the workmen then jumps into the tub and by moving the hide about with his feet soaks it thoroughly with the liquor, in which it is then left for at least eight days, the operation of treading with the feet being repeated. The hide is now taken from the tub and hung up to dry, and when dry is stretched and "fatted" in by the following method:—The hide is warmed by being held over a charcoal fire, and when warm is rubbed on the hair as well as on the flesh side with molten tallow, of which some 3 kilos. are used for every hide. When thirty hides have been thus treated, they are one by one again held and moved to and fro over the fire, and next hung up in the open air to dry. The tallow partly combines with the hide.

The hides thus prepared are converted into a leather of excellent quality, especially suited for the harness of horses and saddlery work of a more common kind, in which, as in that used for artillery horses, great strength is required. This leather is cheap on account of its being prepared in a short time.

(3) *Glove Leather.*—The so-called Erlanger, or French tawing process, is employed only for the production of the glacé, or kid leather, used for making gloves and ball-room shoes. The hair side of the skins intended to be converted into this leather is left unchanged, while as regards wash-leather gloves which are treated (tanned) with fish-oil the hair side is cut off. The skins intended to be converted into kid leather are treated with extraordinary care, and thus acquire in a very high degree all the good quality of alum-tanned (or rather tawed) leather. As these skins are often intended to remain white or are dyed with delicate colours, the greatest care is taken to prevent any injury, as, for instance, contact with oak wood or with iron while wet.

Two kinds of skins are employed for conversion into the better varieties of kid leather; one of these, the more expensive, being the skins of young goats, fed solely with milk, the other being lambskin. Each of these skins yields on an average two pairs of gloves. The leather of which ladies' ball-room shoes are made is obtained from the hides of young calves (so-called calf kid). The preliminary operations of preparing this leather are exactly similar to those already described for the ordinary white leather; but the tawing operations are quite different, the skins being put into a peculiar mixture, by which they are not only tawed, but simultaneously impregnated with a sufficient quantity of oil to render them soft and give suppleness. The mixture consists of a paste composed of wheaten flour, yolks of eggs, alum, common salt, and water. The flour, by the gluten it contains, aids the absorption of the alumina compound, and thus assists the real tawing. The starch does not enter into the composition of the skins, while the yolk of eggs acts by the oil it naturally contains in the state of emulsion, this oil giving to the kid leather that suppleness and softness which is so much esteemed in gloves. It appears that emulsions made with almond oil (the so-called sweet oil of almonds—a fixed oil), olive oil, fish oil, and even paraffine may be advantageously substituted for yolk of eggs. The skins are thoroughly soaked and kneaded in this mixture, to which, in France, there is sometimes added from 2 to 3 per

cent. of carbolic acid for the purpose of preventing the too strong heating of the skins when impregnated with the mixture and packed in heaps. The skins are next stretched by hand and dried as rapidly as possible by exposure to air. Having been damped, a dozen of the skins are placed between linen cloths and trodden upon to render them soft. After this they are, one by one, planed, dried, and again planed. Either by rubbing with a heavy polished glass disc or by the *appreteur*, simultaneously with the application of some white of egg, or a solution of gum, or of fine soap, a gloss is given to the skins, the hair side of which is the right side or dyed side. The dyes are applied either by immersion or by brushing over the leather; the latter, or English method of dyeing skins, is more ordinarily practised.

According to Knapp's researches very good white kid leather is obtained by tawing the epidermis (*blöss*) from lamb- or goat-skins in a saturated solution of stearic acid in alcohol. The leather thus obtained is very soft, has a whiter colour than ordinary glacé leather, and a beautiful gloss.

(4) *Knapp's Leather.*—The preparation of leather with the aid of insoluble soaps, introduced by Knapp, would appear to have become of some importance. The property possessed by oxide of iron of acting as a tanning material has been known for a long time, and in 1855 Mr. Belford took out a patent in this country for a mineral tan method, in which oxide of iron was used; but good leather did not result. The hides do not become really tanned by being immersed in solutions of such metallic salts as those of the ferrous and ferric oxides, and zinc and chromium oxides; for though the acidity of these solutions is reduced to a minimum without producing a permanent precipitate, and thereby the deleterious action of the acid upon the fibres of the hides decreased, and though a certain combination of the oxide and fibres takes place, no real leather is formed because the substance when finished is not fitted for contact with water, for then the so-called tanning is washed out. Knapp's process also is not really a tanning but a tawing operation, by which the skins are alternately immersed in a solution containing from 3 to 5 per cent. of soft soap, and then in a saline solution of oxide of iron, or of chromium, containing 5 per cent. of the salt, from which an insoluble metallic soap is precipitated and impregnated with the fibres. After this operation has been several times repeated the hides or skins are washed in water and dried. Although the exterior colour of good sound leather may be imitated, the real qualities of leather are wanting. Knapp's process is not in use or is so entirely modified by substituting alum for metallic oxides that the skins are tawed by a combination of the preceding tawing processes and the oil-tawing process now to be described.

Iron-tanning is hitherto without practical importance and Heinzerling's chrome tanning is, in the opinion of the author, perfectly worthless.

Electrical Tanning.—The novel process of electrical tanning, patented by MM. Worms and Balé, and worked in this country by the British Tanning Company, Limited, makes use of ordinary tan-liquors, but the tannin is made to act upon the hides by means of an electrical current. At a demonstration of the process which took place in May, 1890, at Rothsay Street, Bermondsey, the visitors were first shown a drum containing tan liquor of the required strength, into which a pack of Australian salted hides, unhaired and cleaned in the ordinary way, were put. The drums employed are 11 feet 6 inches in diameter by 8 feet wide, and contain an electrode running round the interior of one end or head, from which the current passes through the liquor to a similar conductor in the other head.

The drum was set in motion, and a current of 10 ampères passed through the liquor. The action of the current which is applied is partly to *promote diffusion* and partly *to electrolyse the liquor*, both these effects, aided by the rotation of the drum, are no doubt the explanation of the remarkable saving of time effected by this process, it

being possible thus to tan skins and hides in from 24 to 144 hours, against from four to fifteen months by the old process of steeping in pits. A drum was opened which had been running for a little over five days, sections of the hides (salted Australian) were cut and examined by tanners present, and found to be thoroughly tanned. The visitors then inspected the drying sheds and shops above, where leather was seen in all stages, rolled for sole leather, curried, &c., also some hides prepared for machine belting, of which, according to some tests shown us by Mr. Conrad Falkenstein, manager at Rothsay Street, the tensile strength before breaking, taking the average from a number of samples, was equivalent to 4305 lbs. per square inch for the electrically tanned leather, against 3570 to 3800 for leather tanned by the ordinary process. The leather is now being sold in the market, and is steadily taking its place in every branch of the trade.

Oil-Tawing and Wash-leather Process.—By this name is understood a peculiar process by which the skins and hides of various animals, such as harts, deer, sheep, calves, oxen (for the white leather for military use as belts, &c.), are converted into so-called oil- or wash-leather. The tanning material is oil, fat, tallow, or fish oil, to which there has been recently added from 4 to 7 per cent. of carbolic acid. The leather thus obtained is chiefly used for making military breeches, socks, vests, gloves, braces, belts, and surgical appliances, a not inconsiderable quantity being also used, owing to its softness, for washing glass and porcelain. On this account wash-leather is also largely used by gold- and silversmiths for polishing trinkets with rouge (very carefully prepared oxide of iron). The upper or exterior layer of the corium, which owing to its greater compactness does not possess the ductility and suppleness of the lower or interior layer, is in the skins intended to be converted into wash-leather entirely cut away, so that no hair and flesh side are taken into consideration. The cutting away of this layer greatly promotes the absorption of the oil, which by the joint action of air and heat yields a product which is a dry compound of fibre and oil, in which the latter physically has disappeared, inasmuch as the leather is not impervious to water. Wash-leather differs in this respect from oil or fat leather; still, on immersion in water, the skin does not glue together and shrink. Thin skins, such as those of goats and lambs, are not deprived of their hair side, because it would render them too thin for use.

The skins intended to be made into wash-leather are, as regards the first stage of the operation, treated exactly as described for the skins treated with alum, the only difference being that the hair is removed together with the hair side portion of the skins, which are next placed in a bran bath in order to remove the lime. After this the skins are stretched and conveyed to the fulling machine in order to become saturated with oil, for which purpose the skins are first laid on a table or bench and are rubbed with oil, the hair side being placed uppermost. This having been done they are made into clouts and placed under the stampers of a machine so as to thoroughly impregnate them with oil. From time to time the skins are taken from the trough and exposed to the air, then again rubbed with oil and put under the stampers until enough oil has been absorbed. By the repeated exposure to air the skins become dry, and oil (fish oil is chiefly used) absorbed; the exposure to air is continued until the surface of the skins appears quite dry. When the skins have an odour somewhat similar to that of horse-radish, and have lost their fleshy odour, they have absorbed a sufficient quantity of oil, while a portion of the oil has been somewhat changed and has entered into combination with the fibre, another portion only mechanically adhering to the pores of the skins. The next operation therefore aims at rendering the process of the combination of the oil with the skins more rapid by bringing about a fermentation attended with an elevation of temperature; this is effected by placing the skins in a warm room, heaping them together, and covering them with canvas to keep in the heat which is generated, care being taken to air the

heap from time to time in order to prevent overheating and consequent deterioration of the skins. This operation of airing the skins is repeated until by the spontaneous heating they have acquired a yellow colour and the workmen know by experience that the oxidation of the oil is finished. A portion of the oil (estimated at about 50 per cent. of the quantity originally employed) is left in the skins in uncombined state, and is removed by washing with a tepid solution of potash. From this liquor there separates on being left at rest a portion of fat termed *dégras*, and which, as already mentioned, is employed for the dressing of tanned hides. The skins having been thus deprived of the excess of oil are wrung out, dried, and next dressed, in order to restore to them their softness and suppleness partly lost in the drying. Cordovan or Turkey leather, is oil-tawed without the hair side having been first removed, while the flesh side is blackened in the usual way. This kind of leather is chiefly used for ladies' boots and shoes. According to Knapp, skins from which the hair has been first removed may be tawed by treating them alternately with a solution of soap and dilute acids, so that the fatty acids are precipitated into the fibre. After the tawing the skins thus treated should be thoroughly washed in water to remove all acid. As regards the constitution of the leather, commonly known as wash-leather, tawed with oil, nothing is definitely known, but it would appear that this process of tawing has some analogy to the process of imparting oil to calico intended for Turkey-red dying.

Parchment.—The substance known as parchment is not really leather, because its fibres are neither tanned nor tawed, as proved by the fact that boiling water readily converts parchment into a superior kind of glue similar to isinglass, of course too expensive for joiners' use. Parchment is essentially the well-cleansed and carefully dried skins of hares, rabbits, and especially of calves and sheep.

Ordinary parchment is prepared from sheepskins, but the variety known as vellum, *Vélin* or *Parchemin vierge*, is far finer, and is made from the skins of young calves, goats, and stillborn lambs. According to the use intended to be made of parchment, so is its preparation modified. The skins are first soaked in water and then placed in the lime-pits. Sheepskins are cleansed by working with cream of lime in order to preserve the wool. When the hair has been removed the skins are washed, being placed on the dresser's block, and usually also planed with a sharp knife to remove the superfluous fleshy parts. This having been done, each skin is separately stretched in a frame, in a manner very similar to that in use for so-called Berlin-wool work, the skins being held in position by means of strings, and dried by exposure in the open air. Parchment intended for drum skins (from calves' skins), for kettle-drums (from asses' skins), does not require any further operation. If intended for bookbinding the parchment is treated as described, but after drying it is planed with a tool the cutting edge of which is somewhat bent in order to impart a rough surface, whereby the parchment is rendered capable of being written on and dyed. If the parchment be intended—as it was frequently before the invention of metallic paper—for memoranda written with lead pencils, to be wiped out if desired with a wet sponge, it is after planing painted over with a thin white lead paint, for which a mixture of glue water with baryta or zinc white is often substituted. The vellum of this country is generally obtained from sheepskins, which are split into two sheets by means of cutting-tools. Parchment, after having been dried on the frames, is dusted over with chalk and rubbed with pumice-stone. The sieves used in powder mills for granulating the powder are made of parchment obtained from hogs' skins.

Shagreen.—Genuine Oriental shagreen (saghir, sagri, sagre) is a variety of tawed parchment, one side of which is covered with small hard grains. This material is manufactured in Persia, at Astrakan, in Turkey, and in Roumania, from certain portions of the skins and hides of wild asses, horses, and other animals. The hides are soaked in water until the epidermis can be removed easily together with the hairs by

the aid of a dressing-knife; next, the hides are again placed in water so as to swell the material sufficiently to admit of cleansing it, and cutting away on both flesh and hair side all superfluous material, so as to leave only the corium, which then has the appearance of a fresh bladder. In order to produce on skins thus prepared a grained surface, they are put into frames, as described under Parchment, while on the hair side, *allabuta*, the hard black seed of the *Chenopodium album* is stamped in, either by the feet or forced in by pressure. When the skins are dry they are removed from the frame, the seed shaken off, and the skins thoroughly planed with a sharp dressing-knife, then put again into water, tawed, and finally dyed. The tawing is effected by the aid either of alum or of oak bark. The dye of shagreen is generally green, and is due to salts of copper. After dyeing the skins are soaked in mutton tallow.

Fish skin, or fish shagreen, is obtained from various kinds of sharks (*Squalus canicula*, *S. catulus*, *S. centrina*) and other fishes of the same class. The skin of these animals is not covered with scales, but with more or less projecting hard points. The skins having been removed from the fish are stretched in frames and simply dried, being then sent to the market. Formerly sharks' skin was in some countries used by joiners instead of sand- and glass-paper for preparing wood. The skins deprived of the projections are dyed and used for covering small boxes, tubes of small telescopes, &c.*

GLUE, SIZE, GELATINE.

General Observations.—The organisms of all animals, but more especially of the higher classes, contain tissues which are insoluble in cold as well as in hot water, but which by continued boiling become dissolved, and yield on evaporation of the solution a glutinous gelatinising mass, which, by further drying, exhibits, according to the degree of purity of the material, a more or less transparent and brittle substance, which in its pure state is devoid of colour as well as of smell, becoming swollen in cold water and dissolved by boiling in that liquid. This substance—*i.e.*, the product of the conversion of the so-called glue- or gelatine-yielding tissues, is what is known in the trade as glue, and is largely used by carpenters, joiners, &c., for joining wood. It is also largely used for sizing paper, for clarifying various liquids—beer and wine, for instance—and as a cement. Among the glue-yielding tissues the following are the most important:—Cellular tissue, the corium, tendons or sinews, the middle membrane of the vasa lymphatica and veins, the osseine or organic matter of bones, hartshorn, cartilage, the air bladders of many kinds of fish, &c. Chemically, we distinguish between glutin, that is to say, glue derived from skins, bones, &c., and chondrin, which has been obtained from cartilage. From a technical point of view this distinction is hardly required, as the cartilaginous matter is as much as possible eliminated from other glue-making materials, because experience has shown that glutin has a much greater power of adhesion than chondrin. The latter, however, is largely used as size in this country.

As already observed, the glue or gelatine-yielding tissues yield on being dissolved a gelatinising mass, the aqueous solution of which does not, however, possess to any great extent a glueing property, which is only imparted to the gelatine by a process of drying. In considering, therefore, the process of glue-boiling, we have to distinguish the animal matter capable of yielding glue, the gelatinous mass obtained therefrom, and the glue obtained by drying the latter. The temperature required for producing gelatine differs according to the different animal tissues employed; the consistency of the gelatine obtained from equally strong solutions varies with the age of the tissues operated upon.

* The reader may further consult *Leather Manufacture*, by A. Watt (London: Crosby Lockwood & Co.); *Text-Book of Tanning*, by H. R. Procter (London: C. & F. N. Spon).

Glue readily dissolves by boiling in water, forming on cooling a gelatinous mass, even if the quantity of glue is only 1 per cent. Repeated boiling and cooling a glue solution causes it to lose the quality of gelatinising, and the same effect is produced by acetic and dilute nitric acids. Solutions of alum precipitate glue solutions only after the addition of potash or soda, the precipitate consisting of glue mixed with basic aluminium sulphate. Glue enters with tannic acid into a combination of constant composition; hence glue or gelatine may be used for the estimation of tannin in vegetable matter.

Three different kinds of glue are distinguished by the manufacturers, viz.:—

(*a*) So-called skin-glue, or leather-glue, prepared from refuse hides, skins tendons, &c.

(*b*) The glue obtained from bones.

(*c*) The glue obtained from fish-bladders, termed isinglass.

Very recently glue from vegetable gluten and so-called albumen glue have been prepared.

Leather Glue.—This substance is prepared from a large variety of animal refuse, the chief sources being the following:—Refuse from tanyards, tawing and leather-dressing works, old gloves, rabbit and hare skins (the hair having been used by hatmakers), skins of cats and dogs, ox feet, parchment cuttings, surons (skins which have served the purpose of carrying drugs, especially from America), sinews, gut, leather cuttings (leather tanned with oak bark cannot be readily converted into glue). The glue-boiler on an average obtains from the various materials about 25 per cent. of glue, preference being given to the refuse of tawing operations and kid leather making, because these materials are ready for boiling without requiring any previous treatment. Glue-boiling involves the following operations:—

(1) Treating the glue-yielding materials with lime.

(2) Boiling these materials.

(3) Forming the gelatine.

(4) Drying the gelatine so as to form glue.

(1) *Treating with Lime.*—The aim of this operation is the cleansing of the refuse and the prevention of putrefaction. It is effected by placing the cuttings in tanks or lime-pits and pouring in a thin milk of lime. The materials, while the milk of lime is frequently renewed, are thoroughly mixed with the lime-liquid and left for fifteen to twenty days in the pits. By the action of the lime any blood and flesh is dissolved and the fatty matter saponified. In order to remove the excess of lime, the materials are placed either in nets or willow baskets, and these are immersed in a brook or river, where a continuous stream of fresh water removes the greater part of the lime in a few days. The washed material is next exposed in the yard to the action of the air in order that it may become dry, as well as form a carbonate of any lime still present in the materials. When the materials are dry they are packed and sent off to the glue-boilers, who, previous to proceeding with the boiling operation, macerate the materials again in a weak milk of lime, the maceration being followed by washing.

Fleck states that a weak alkaline lye (5 kilos. of soda ash and 7·5 kilos. of quicklime to 750 to 1000 kilos. of glue-yielding material) is preferable to the use of milk of lime. When the glue-boiling and tanning operations are executed on the same premises, the lime-treated glue materials are put for a few hours into old oak bark liquor, the acids (lactic, butyric, and propionic acids) of which remove the lime, while the animal matter is at the same time superficially tanned. This glue tannate rises during the boiling as scum to the surface, and assists in rendering the glue liquor clear. According to Dullo, the Cologne glue—a very pale and strong glue—is obtained

from offal, which, after liming, has been treated with a solution of chloride of lime (calcium hypochlorite), and thereby bleached.

Boiling the Materials.—This operation is carried on either in the ordinary manner of boiling anything with water, or by so-called fractionated boiling, or finally by the application of steam. As the conversion of the glue-yielding materials into glue takes place slowly and gradually under the influence of the boiling-water, it is clear that the method of boiling cannot be without influence upon the glue ultimately produced. The first portions of gelatine which are formed remain in contact with a boiling-hot mass, and are thereby further changed so as to lose the capability of gelatinising, while the glue at last obtained exhibits a dark colour, and is often not so strong, although it is generally believed that deep-coloured glue is of a better quality. A rational mode of glue-boiling would involve the gradual removal of the solution obtained, while of course fresh water would have to be supplied to replace the liquor drawn off. The older method of glue-boiling consists in simply placing the materials with water in a cauldron, care being taken to prevent burning by placing them on a stout wire gauze or tying them in a net and suspending it in the boiling liquid. Soft water yields a better result than hard. Gradually the materials become dissolved, and the scum which is formed is taken from the surface with a large ladle. The refuse of glue of former operations is added to the boiling liquid, and the operation continued until the liquid is of the required strength, which is tested by pouring into a broken egg-shell a small portion of the liquor, and by placing the partly-filled shell in ice-cold water. If the solution gelatinises after a while, forming a hard and rather stiff gelatine, the liquor is run off by means of a tap, filtered through a layer of straw placed in a basket, and conveyed to a wooden lead-lined cistern, externally covered with mats or straw, or some bad conductor of heat. In some works the liquor is decanted into a deep but narrow boiler, the furnace of which is so arranged as to impart heat to the top of the vessel only. This vessel, as well as the cistern, is heated previously to the liquor being poured in. The liquor is clarified by stirring into it a small quantity of very finely-pulverised alum, 0·07 to 0·15 per cent., into the liquid. After this the liquid is left to stand all night. The alum precipitates any lime remaining as calcium sulphate, and also some organic matter which renders the liquid turbid. Alum, though it prevents the putrefaction of the glue while drying, impairs its strength. The lime might better be precipitated by oxalic acid, and the organic matter removed by adding to the boiling mass some astringent matter, such as oak bark decoction or hops, so that during the boiling the organic impurities could be taken away as scum.

Fractionated Boiling.—By this operation only a comparatively small quantity of water is added to the animal matter intended to be converted into glue. When the water is fairly boiling the cauldron is covered with a well-fitting lid, and the steam being kept in as much as possible, is allowed to act upon the materials so as to convert them into glue. When, after continued boiling for about two hours, the water has taken up sufficient gelatine, the liquor is run off and fresh water poured on the materials. This operation is repeated until the decoction no longer gelatinises, the last liquor being kept instead of water for use for a following operation. The liquors thus obtained, excepting the last, are either mixed or each is treated separately. The glue yielded by the first decoction is stronger than that yielded by the subsequent liquors. By this method of boiling the saturated liquor does not remain exposed to the action of heat and water too long, and consequently a better article is produced. In some instances the materials intended to be converted into glue are boiled in a vessel similar in construction to those in use in bleaching-works and in paper-mills, arranged in the following manner. At some distance from the bottom a perforated false bottom is placed, in the centre of which is fixed a wide tube which reaches to

about two-thirds of the height of the cauldron. The materials intended to be converted into glue are placed upon the perforated bottom, and water under it; as soon as the water boils, the steam produced, not being able to escape rapidly and readily through the materials, exerts a pressure upon the liquid, and forces it through the tube, the consequence being a constant stream of boiling liquid falls upon the glue materials, which are rapidly dissolved.

A more rational mode of conducting this operation consists in employing high-pressure steam, admitted into the mass of the animal materials to be converted into glue. In this manner a very concentrated solution of glue is obtained in a short time. In England steam is generally employed, but on the Continent its use is the exception. It has been said that it is advantageous to allow the animal offal intended for glue to become somewhat decomposed, and then to disinfect it with chlorine or sulphurous acid before boiling it for glue, because by this mode of treatment a brighter glue is obtained. We are unable to say whether this opinion is correct.

Moulding.—As soon as the glue solution has, by standing in the tanks into which it had been transferred from the boilers, become quite clear and somewhat cooled, the liquid is poured into moulds, and when solidified the jelly is cut into cakes of the shape and size met with in the trade.

The moulds, into which the glue solution is poured through a strainer made of metal gauze, are of wood, and generally a little wider at the top than at the bottom, so as to admit of an easy removal of the solid material. At the bottom of the moulds a series of grooves are cut at such a distance from each other as agrees with the size of the intended glue-cakes. Before the liquid is poured into the moulds, these are thoroughly washed, and either allowed to remain damp, or if dried, are oiled, so as to prevent the solidifying gelatine adhering to the wood. Recently moulds made of sheet-iron and zinc have been introduced. The moulds are filled with the lukewarm glue solution, and when the glue is sufficiently hard it is gently loosened from the sides with a sharp tool, and the mould having been turned over on a wooden or stone table, previously damped, is lifted off the block of gelatine, which is next cut into cakes or slabs. The cutting-tool is simply a piano-wire, or more frequently a series of these stretched in a frame at sufficient distance from each other to make the cakes of the desired thickness, the frame being placed on small wheels so as to be easily moved. Glue is met with in the trade as a gelatinous mass, or is sold in casks under the name of size. It is said that the process of drying impairs the good qualities of the glue.

Drying the Glue.—This operation is performed by placing the gelatine cakes on nets made of twine stretched in frames, and exposed in a dry airy place to the action of the sun. The drying is one of the most difficult operations of the glue-making process, because the temperature of the air and its hygrometric condition exert a great influence on the product, especially during the first few days.* The glue will not bear a temperature above 20°, because at a higher temperature it becomes again fluid, and as a matter of course flows through the meshes of the net and adheres to the twine so strongly as to require the nets to be put into hot water for the removal of the mass. Air too dry causes an irregularity in the drying of the glue, and as a consequence the cakes become bent and cracked; while frost causes disintegration, so as to necessitate a re-melting of the glue: hence it follows that drying in the open air can only be effected in the spring and autumn. Although the glue-boilers have tried to dry glue by artificial heat, this plan has not been generally introduced owing to the fact that a slight excess of heat causes the melting of the gelatine, the more readily when ventilation is neglected. Drying-rooms, as recently constructed, are large-sized

* It is very generally considered that the occurrence of a thunderstorm during the process of drying renders it necessary to remelt the product.—[EDITOR.]

sheds fitted with the required frame-work for receiving the gelatine cakes, and heated by steam-pipes placed on the floor near the latter. The walls are provided with openings which can be closed by means of valves, while there are ventilators in the roof arranged to obtain a proper circulation of air. As the gelatine placed nearest to the floor of the room becomes most quickly dry, it is, with the frames upon which it placed, removed after eighteen to twenty-four hours to a higher part of the drying-room, which is not heated at all if the outer air has a temperature of from 15° to 20°. The drying-shed, or room, is by preference built so as to face the north. When the glue has been thus dried as much as possible, it is generally quickly dried in a stove in order to impart hardness. It is next polished by being immersed in hot water, and cleaned with a brush, and again dried.

Bone-Glue.—The organic matter contained in bones, forming nearly one-third part (32·17 per cent.) of their weight, consists of a material which, after the bones have been treated with hydrochloric acid, is very readily converted into glue by the action of high-pressure steam. The preparation of glue from bones by the action of hydrochloric acid is the usual mode of proceeding, and the operation is advantageously combined with the making of sal ammoniac and phosphorus.

The preparation of glue from bones includes the following operations:—

(1) *Boiling out the Grease.*—The bones are put into water and boiled in a cauldron, the fat floating to the surface. Frequently, in order to save fuel, the bones are put into an iron wire basket, which is removed after the boiling has been continued for some time, the bones thrown out and fresh ones put in, the boiling being continued until a thick gelatinous liquor is obtained. The fat or grease is removed from the surface of the liquid by means of ladles. The gelatinous mass obtained by this process is either used as a manure or is given to cattle as fodder! In some works bones have been exhausted with carbon disulphide for the purpose of extracting the grease.

(2) *Treating the Bones with Hydrochloric Acid.*—The bones, having been drained, are placed in baskets, and in these are immersed in tanks to more than half their height, the tanks being filled with hydrochloric acid at 9·6° Tw. (= 1·05 sp. gr. = 10·6 per cent. ClH); 10 kilos. of bones require 40 litres of acid. The bones are kept in this liquor until they become quite soft and transparent. They are next drained, and then, with the baskets, immersed in a stream or brook with a good supply of running water to wash out the greater portion of the acid,* which is fully neutralised by placing the bones in lime-water, again followed by washing with fresh water, the bones being then ready for boiling. Gerland has suggested the use of sulphurous instead of hydrochloric acid.

(3) *Conversion of the Organic Matter into Glue.*—The cartilaginous substance having been either partly or completely dried is put into a cylindrical vessel containing a false perforated bottom, and between that and the real bottom a pipe or tube. To the top of the vessel a lid is fitted, provided with an opening for a steam-pipe leading from a small boiler. Shortly after the admission of the steam a concentrated glue solution begins to run off from the pipe at the bottom of the cylinder; this solution is usually so concentrated as to admit of being at once run into the moulds, and, after having become solid, is treated as before described. After a few hours a weak liquid makes its appearance, and as soon as this happens the cylindrical vessel is opened, the glue mass removed with the weak liquid to a copper and boiled, care being taken to stir the magma constantly. As soon as the glue is dissolved the liquor is poured into moulds. Glue obtained from bones exhibits a milky appearance, due to the presence of a small quantity of calcium phosphate retained in the substance. Sometimes there is purposely

* This method of washing pollutes the streams, and is no longer permissible where due sanitary inspection is enforced.—[EDITOR]

added more or less baryta-white, zinc-white, white-lead, chalk, or pipe-clay. The glue obtained from bones is sold under the name of patent glue.

Liquid Glue.—When glue is dissolved in its own weight of water and a small quantity of nitric acid added to the solution, it loses the property of gelatinising, while the adhesive property of the glue is not impaired. Dumoulin prefers to dissolve 1 kilo. of Cologne glue in 1 litre of boiling water, and to add to the solution 0·2 kilo. of nitric acid at 62° Tw. = 1·31 sp. gr. After the evolution of the nitrous acid fumes has subsided the fluid is cooled. A better liquid glue is obtained by dissolving good gelatine or glue of superior quality in strong vinegar or moderately strong acetic acid, to which some pulverised alum and one-fourth of its bulk of alcohol are added, the solution being aided by a water-bath. The action of the acetic acid is the same as that of the nitric acid. According to Knaffl, a very excellent liquid glue is obtained by heating for some 10 to 12 hours upon a water-bath, a mixture of 3 parts of glue in 8 parts of water, to which are added 0·5 part of hydrochloric acid, and 0·75 part of zinc sulphate, the temperature of the mixture being kept below 85°. This kind of liquid glue keeps for a very long time and is largely used for joining wood, horn, and mother-of-pearl. This glue is employed by the makers of artificial pearls.

Tests of Quality of Glue.—Although the quality of glue is best ascertained by practical use, some of the physical qualities and the external appearance of glue may be mentioned as indicating a superior article. Glue of good quality should exhibit a bright brown or brown-yellow colour, should be free from specks, glossy, perfectly clear, brittle, and hard, should not become damp by exposure to air; when being bent it should snap or break sharply, the fracture presenting a glassy, shining appearance. When placed in cold water glue should not even after remaining forty-eight hours in this fluid swell up and increase in bulk nor dissolve. A splintery fracture of glue indicates that it has not been well boiled. The adhesive property of glue is often increased by adding certain pulverulent earthy substances. This addition is regularly the case with Russian glue. Among the substances employed are white lead, lead sulphate, zinc white, baryta white, and even lead chromate. As different kinds of glue may agree in their external aspect and yet vary as regards their adhesive power, methods of testing glue have been proposed, some of which are based upon the chemical, others upon the physical, properties of this substance.

Chemical tests are less decisive than mechanical trials. Lipowitz dissolves 5 parts of the glue in so much hot water that the weight of the solution makes up 50 parts and allows the solution to stand for twelve hours at a temperature of 18°, in order to gelatinise. On the top of an open glass of uniform width, he lays a slip of tin plate, through the middle of which passes a perpendicular wire, a cup-shaped piece of tin with its convex side outwards being soldered to its lower end. The wire with the cup weighs 5 grammes and moves freely in the tin plate. To the top of the perpendicular wire is fixed a funnel which also weighs 5 grammes and into which there may be poured fine shot up to the weight of 50 grammes. According to the greater aptitude of the glue to form a solid jelly the apparatus must be the more heavily weighted in order to sink into the jelly, whence the tenacity of the glue may be approximately calculated.

Karmarsch simply glues two pieces of wood together and determines the weight required to break them asunder. Weidenbusch saturates rods of plaster of Paris with glue and breaks them. Bauschinger glues two pieces of red beech-wood together in such a manner that their fibres run parallel and that each projects one centimetre beyond the other, the glued surface being 10 × 10 = 100 square centimetres. When thoroughly dry these pieces are fixed in Werder's testing machine in such a manner that its steel cheeks catch in the retreating angles formed by the projecting parts of the pieces of wood, just at the beginning of the glued joint. On seeking to move these

angles towards each other by a measured and gradually increasing force, the glued surfaces of the pieces of wood were at last pushed over each other and in this manner the resistance to a lateral pressure was measured in kilos. and square centigrammes.

Horn determined the resistance of common glue to a tearing force as 9·6 kilos., that of Cologne glue as 10·6, and that of gelatine as 31·5 kilos.

Kissling found in glue 12·3 to 18 per cent. of water, 1·4 to 5·1 per cent. of ash, 0 to 0·8 per cent. of a volatile acid, and 0 to 40 per cent. of matter insoluble in water.

SIZES.

Coarse glues are used in finishing, and to some extent in dyeing, textile goods, in order to increase their body, stiffness and gloss. The kinds occurring in commerce are bone-size and glue-size.

The best bone-size is made from the "sloughs" of the horns of oxen. Of these 4 cwts. are boiled for ten hours. The liquid is strained, and then are added, with vigorous stirring, alum 3 lbs., and zinc sulphate 2 lbs., both in fine powder. The solution is received in shallow tubs and allowed to cool. The yield from the above proportions is 10 cwt. It keeps for eighteen months.

It is pale, clear, and semi-transparent. Its adhesive power is less than that of the glue size made from the clippings of hides.

Glue size is a dark brown, stiff semi-solid mass of great tenacity. It is frequently contaminated with the exuviæ of the larvæ of blow-flies, which adhere to the goods and render them unsightly. Hence glue size should be preferably made in winter, and be kept in cold, dark, but draughty places.

Isinglass, Fish Glue.—The substance met in commerce under the name of isinglass is, if genuine, the dried interior pulpy vesicular membrane of the air-bladder of certain kinds of fish belonging to the order of the cartilaginous ganoids, and more especially of the common sturgeon (*Accipenser sturio*); the huso, or grand sturgeon (*A. huso*); the *A. Güldenstaedti* and *A. stellatus*. The bladders of these and of kindred species of fish, plentifully met with in the Caspian Sea and the estuaries of the rivers running into it, are cut open, cleansed, stretched, and dried by exposure to sunlight, and when sufficiently dry to admit of being handled without fear of tearing the outer muscular membrane, which does not yield any glue on being boiled, is torn off, while the interior membrane is moulded in various ways (as in rings, lyre-shaped, or folded as leaves of paper), and bleached by sulphurous acid, then thoroughly dried by exposure to sunlight.

According to the countries from which it is sent into the trade, isinglass is distinguished—as Russian (the best kind being obtained from Astrakan); North America (from *Gadus melucius*); East Indian (from *Polynemus plebejus*), met with in leaves, also in small sacks, and in the entire bladder; Hudson's Bay isinglass (derived from sturgeons); Brazilian is probably obtained from various kinds of *Silurus* and *Pimeladus*. This isinglass is met with in commerce in hollow tubes, in lumps, and in discs. German isinglass is prepared at Hamburg from the air-bladder of the common sturgeon. In Roumania and Servia the skin and intestines (not the liver) of cartilaginous fishes are boiled into a stiff jelly, which, having been cut into thin slices, is dried and sent into the market as isinglass. As regards the use of this material, we have to distinguish between fish glue and isinglass. The former, if properly prepared, is not at all distinguishable from ordinary glue as obtained from bones or other animal refuse; but isinglass is not glue, and is only converted into it by boiling. It consists of fibres or threads, which when placed in water are somewhat dissolved, but retain their organised structure; this being especially of importance for the use of this substance in clarifying wine, beer, and similar fluids, as the fibres

constitute as it were a close network, which readily takes up the turbidity produced by small particles. The presence of tannin in liquids which are intended to be clarified by the use of isinglass is advantageous, inasmuch as it promotes the contraction of the isinglass fibres, whereby the suspended particles present in the fluid to be clarified are retained; so that in truth the clarifying by isinglass is a kind of filtration, which cannot be performed either by glue or by a hot saturated solution of isinglass. For isinglass, in all other instances, such as the dressing of woven silk fabrics, the preparation of so-called court-plaster and cements, there may be substituted good gelatine. Under the name of *Ichthyocolle française*, Rohart some years ago introduced a substitute for isinglass, a compound said to be obtained from fibrin of blood and tannin.

Substitutes for Glue.—Recently three substitutes for glue have been introduced, viz.:—(1) Gluten glue (*colle gluten*). (2) Albumen glue (*colle végétale ou albuminoide*). (3) Casein glue (*colle caséine*). The first is a mixture of gluten and fermented flour. It is a very sour mixture, endowed with but very slight adhesive power. Albumen glue is partially decayed gluten, the substance largely obtained in the manufacture of starch from wheaten flour thoroughly washed with water, and then exposed to a temperature of from 15° to 20°, at which it begins to ferment and become partly fluid, or more correctly soft, so as to admit of being poured into moulds, which are placed in a room heated to 25° or 30° for from twenty-four to forty-eight hours. The surface having become dry enough to admit of the cakes being handled, they are taken from the moulds and further dried by being placed either on canvas or on wire gauze. After four or five days the cakes are quite dry and fit for being kept in a dry place for any length of time. A solution of this substance in twice its weight of water constitutes a normal solution, which may be used for the following purposes:—Glueing wood, cementing glass, porcelain, earthenware, mother-of-pearl, for pasting leather, paper, and cardboard; it may further serve as weaver's glue, and as dressing for silk and other woven fabrics; also for a mordant instead of albumen in dyeing and printing various fabrics; and lastly, for clarifying liquids. Casein glue is prepared by dissolving casein in a strong solution of borax. The thick fluid thus obtained has great adhesive powers, and may be advantageously employed by joiners and bookbinders.* What is known as elastic glue is a preparation of glue and glycerine, by the addition of which glue may be rendered permanently elastic and soft. It is prepared in the following manner:—Glue is melted in water, by the aid of a water-bath, into a very thick paste, to which glycerine is added in the same quantity by weight as that of the dry glue. The mixture is thoroughly stirred, and then further heated, in order to evaporate the excess of water. The mass is then cast on a marble slab, and after cooling, serves for the purpose of making printer's inking rollers, elastic figures, galvano-plastic moulds, &c.

BONES.

The bones of animals serve for obtaining phosphorus, as already described, for bone-meal and animal charcoal, bone-black or spodium.

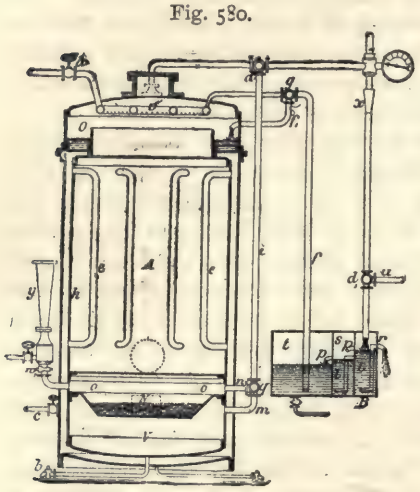
For extracting fat, the bones are either boiled in water or steamed. A great part of the fat separates out, but at the same time a part of the cartilage is dissolved as glue, so that the manurial value of the bones is reduced. The fat extracted by boiling is the best; that obtained by steaming is inferior; whilst the fat extracted by benzene has the lowest value, since soaps prepared from such fat retain the mouldy smell of the bones.

* Skimmed milk, as free from fatty matter as possible, is coagulated by means of weak acetic acid. The curd is well washed, pressed and dissolved, either, as above said, in a concentrated solution of borax, or in sodium silicate (so-called water-glass). The liquid is very useful in getting up ornamental articles, artificial flowers &c.—[EDITOR.]

As only from 3 to 4 per cent. of fat are obtained by boiling, but from 5 to 6 by the benzene process, and as in this latter case there is no loss of glue—*i.e.*, of nitrogen—the extraction by means of benzene is coming more and more into use.

According to Büttner, the recipient, *A* (Fig. 580), is filled with bones; then steam is let into the jacket, *k*, and the pipes, *e*, through the cock, *c*, whereby the moist air formed by heating the bones is sucked out by the steam-blast, *y*, at *o*. The cock, *q*, is then opened into the pipe, *n*, the cock, *d*, to the pipe *i*, the cock, *d*, to the pipe, *u*, and the residual air from the pan, *A*, and from the bones is sucked by the water-blast, *x*, until the air in *A* is sufficiently exhausted, when the cock, *q*, is closed again. On opening the cock, *g*, the benzene in the space, *t*, of the receiver, *B*, rises up in the pipe, *f*, penetrates into the worm, *v* (perforated below), falls in the form of rain upon hot, dry bones free from air, and penetrates into them until they are saturated. The rest of the solvent is let through the pipe, f_1, into the receiver, *O*, and is there evaporated. The vapours of the solvent are now drawn by the aid of the water-blast, *x*, from above downwards through the pan, *A*, the pipe, *n*, the cocks, *q* and *d*, and the pipe, *i*, liquefied on their way from *x* to the receiver, *B*, by the water of the water-blast, and collected along with the water in the space, *r*, of the receiver, *B*. The water flows off chiefly by the pipe, *l*, whilst the pure benzene flows to the space, *t*, in order, after the air-pressure, to rise into the worm, *v*, and the receiver, *O*. When the extraction of the fat is at an end, the solvent is driven out by admitting steam into *k* in the manner described above, and collected in the space, *t*, of the receiver, *B*, in order to be used again. An expansion of air is now produced in the space, *V*, below the bottom, *N*, by opening the cock, *q*, to the pipe, *m*, by means of the water-blast, *x*, the fat on the filtering stratum of the bottom is sucked through, and the pure fat is let off at *b*.

Fig. 580.



In order to extract the glue from the bones, water is let in through the cock, *a*, and the worm, *v*, and steamed till the glue is dissolved. The cock, *q*, is opened into the pipe, *m* and *i*, cock, *d*, steam-blast, *x*, and cock, *d*, opened to *u*, and the steam is let off through *u*.

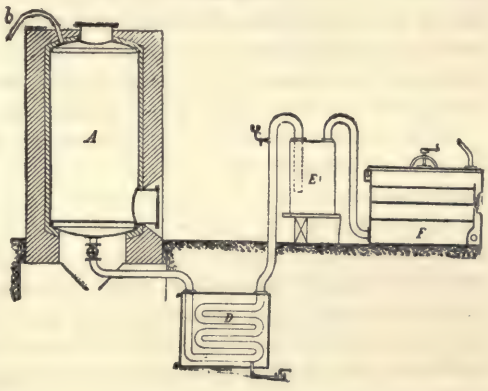
There thus arises a strong current of vapours from above downwards through the pan, *A*, which forcibly sweeps the dissolved glue downwards through *A*, and through the filtering-bed, where it is freed from dirt and particles of bone. When this has been repeated a few times, the bones are freed from gelatine, and the concentration of the glue and the simultaneous drying of the bones may begin in the pan, *A*. For this purpose the space, *k*, is heated by steam under pressure, so that the glue in *V* begins to boil. Lest the temperature in *A* should rise too high, the water-blast, *x*, and the steam-blast, *y*, are set in action, so that these two apparatus draw away the water evaporating from the glue and the bones through the cocks, w_1 and *q*, and the pipes, *n* and *m*, at *o*, the glue is sufficiently thickened. The glue is then run off, and the bones are heated and dried for a short time until the last remnant of moisture is expelled.

Bone-black (*Animal Charcoal*).—The carbonisation of the bones is so conducted that the volatile products are either burnt or condensed. In the latter case the broken-up bones are put into iron retorts similar to those used for coal-gas manufacture, and the

volatile products are collected in suitable condensing apparatus, while the gas after having been purified, is sometimes led into a gas-holder and used for illuminating purposes, or when not purified is burnt under the retorts. According, however, to the experience obtained in Germany, bone-black thus made has a lower decolorising power than when the bones are ignited in iron pots, the volatile products being burnt at the same time. In Germany, therefore, the older plan of carbonisation in pots is usually resorted to. In England and Scotland, and also in Holland, Belgium, and France, retorts are generally used for this purpose. The carbonisation in pots is carried on in the following manner: Cast-iron pots are filled with broken-up bones placed one on the top of the other, the edges of the mouths of the pots being luted with clay. The pots are placed on the hearth of a kind of reverberatory furnace. After awhile the vapours which are forced through the lute become ignited, thereby enveloping the pots in a sheet of flame, so that the carbonisation goes on without requiring the firing of the furnace to be kept up. When the flame subsides the carbonisation is complete. The yield of animal charcoal amounts by this method of procedure to 55 to 60 per cent., the carbonaceous matter being, however, mixed with about ten times its weight of mineral matter, as may be inferred from the following results of analysis of a dried sample of bone-black, which in 100 parts was found to consist of: Carbonaceous matter, 10; calcium phosphate, 84; calcium carbonate, 6 parts. By exposure to air bone-black absorbs from 7 to 10 per cent. of moisture. The carbonised bones are broken up and granulated by machinery, the formation of dust having to be avoided as much as possible because it has very little value.

Zwillinger carbonises bones with superheated steam in a large iron receiver, *A* (Fig. 581), coated with an insulating mass, and secures at the same time the bye-products. Superheated steam is introduced at the pipe, *b*. The vapours given off escape through the refrigerating room, *D*, to the iron washing-vessels, *E*, and the gas-purifier, *F*.

Fig. 581.



Properties of Bone-black.—As far back as the year 1811, Figuier discovered that bone-black possesses the property of withdrawing organic and inorganic substances—viz., lime and potash from solutions. It appears that this property is due to surface attraction (capillary action), although bone-black is also capable of decomposing chemical compounds. Owing to the fact that bone-black can absorb inorganic matter, it is largely used for the purpose of withdrawing lime and saline matter from saccharine fluids in beet-root sugar works. According to Anthon, the property of bone-black to withdraw lime from solutions is partly due to the fact that carbonic acid is condensed in the pores of this substance.

By treating bone-black with hydrochloric acid, and thus dissolving the mineral matter it contains, the residue, after having been well washed with water, dried, and re-ignited in a closed crucible, has lost in a very great measure its property of withdrawing from solutions and retaining within its pores inorganic matter. When acid liquids are to be decolorised by bone-black, it should always be employed after having been treated with hydrochloric acid. Shoe-blacking manufacturers employ in their trade a large quantity of bone-black.

Testing Bone-black.—The greater the decolorising power of charcoal the better its

quality, though it appears that the decolorising power is not proportionate to the power of withdrawing lime and saline matters from solutions. In order to ascertain the decolorising power of any sample of bone-black, its quality in this respect is compared with that of another of known strength. Payen proposes to take equal bulks of water coloured with caramel, to treat these with equal weights of animal charcoal, and to filter these mixtures; the charcoal which yields the clearest liquid being the best. Bussy obtained the following results by the estimation of the relative decolorising power of equal quantities by weight of different kinds of charcoal:—

Ordinary bone black	1·0
Bone-black treated with hydrochloric acid	1·6
„ and afterwards ignited with potassium carbonate	20·0
Blood ignited with potassium carbonate	20·0
„ „ calcium carbonate	20·0
Glue ignited with potassium carbonate	15·5

Brimmeyr's experiments on the decolorising properties of bone-black led to the following results: (1) The capability of absorption of this substance does not depend upon the mechanical structure of the bone-black, but upon the quantity of pure carbon it contains. (2) The quantities of matter absorbed by bone-black of various kinds are —when reduced to pure carbon—really equivalent, and are probably independent of the varying chemical nature of the soluble absorbed substance. (3) Bone-black saturated with any substance retains its absorptive power for other materials of a different chemical nature. (4) Bone-black acts the quicker and better the less its capillary structure has been interfered with either by mechanical or chemical means (action of hydrochloric acid). Schultz's results of experiments agree with those just quoted. The specifically lightest bone-black which contains the largest amount of carbon is the most strongly decolorising material. As regards the sugar (especially beet-root) manufacture, the power of bone-black to withdraw lime from a solution comes also into consideration; this lime-absorbing capability is estimated by directly testing the quantity of lime which a given sample of charcoal can take up.

Revivification (Re-burning) of Charcoal.—After having served the purpose of decolorising and absorbing lime for some time in the process of sugar refining, the bone-black becomes, as it is termed, foul and requires to be revived, for which purpose it is either first thoroughly washed with hot water or sometimes left to enter into a state of fermentation, or treated with steam, and finally always re-ignited. The more usual plan is to wash the bone-black, while still in the filters, with hot water, so as to remove all soluble matter, the material being next re-ignited. In this manner bone-black may be restored for use from twenty to twenty-five times. This mode of reviving labours under the disadvantage that during the ignition the organic matter (absorbed impurities) is not quite destroyed, and by choking the pores of the bone-black impairs its decolorising power. It is therefore preferable to cause the bone-black to ferment, to treat it next with dilute hydrochloric acid, wash it well, and lastly ignite it. The quantity of hydrochloric acid employed for this purpose in sugar-producing works is very large.

Substitutes for Bone-black.—Among the substances which have been tried as substitutes for the use of bone-black, carbonised bituminous shale takes the first place. This material (the coke of the Boghead coal is an excellent example) absorbs colouring matter, but does not touch the lime. Moreover it often happens that the coke is rendered unfit for this use by the presence of a considerable amount of iron monosulphide. The coke of sea-weed is perhaps a more suitable material.*

* A variety of artificial carbons have been prepared by charring mixtures of organic and inorganic matter, but none of them have come into general use.—[EDITOR.]

FATS.

Fats are neutral substances of animal or vegetable origin which leave upon paper a transparent spot which does not disappear on prolonged exposure to the air. They cannot be volatilised without decomposition; their specific gravity is less than that of water, in which they are insoluble, but they dissolve in ether, carbon disulphide, or benzene. Almost all fats, in contradistinction to wax, are triglycerides—*i.e.*, compounds of glycerine, $C_3H_5(OH)_3$, with fatty acids. Berthelot has, *e.g.*, obtained factitious tripalmitine from palmitic acid and glycerine:

$$C_3H_5(OH)_3 + 3H.C_{16}H_{31}O_2 = C_3H_5(C_{16}H_{31}O_2)_3 + 3H_2O,$$

and in like manner trioleine from oleic acid:

$$C_3H_5(OH)_3 + 3H.C_{18}H_{33}O_2 = C_3H_5(C_{18}H_{33}O_2)_3 + 3H_2O.$$

Setting the drying oils aside there are two homologous series of fatty acids: The first series has the general formula $C_nH_{2n}O_2$.

Formic acid	CH_2O_2
Acetic acid	$C_2H_4O_2$
Propionic acid	$C_3H_6O_2$
Butyric acid	$C_4H_8O_2$
Valerianic acid	$C_5H_{10}O_2$
Capronic acid	$C_6H_{12}O_2$
Œnanthylic acid	$C_7H_{14}O_2$
Caprylic acid	$C_8H_{16}O_2$
Pelargonic acid	$C_9H_{18}O_2$
Capric acid	$C_{10}H_{20}O_2$
Lauric acid	$C_{12}H_{24}O_2$
Myristic acid	$C_{14}H_{28}O_2$
Palmitic acid	$C_{16}H_{32}O_2$
Stearic acid	$C_{18}H_{36}O_2$
Arachic acid	$C_{20}H_{40}O_2$
Behenic acid	$C_{22}H_{44}O_2$
Cerotic acid	$C_{27}H_{54}O_2$
Melissic acid	$C_{30}H_{60}O_2$

The second series has the general formula $C_nH_{2n-2}O_2$:

Acrylic acid	$C_3H_4O_2$
Crotonic acid	$C_4H_6O_2$
Angelicic acid	$C_5H_8O_2$
Pyroterebic acid	$C_6H_{10}O_2$
Cyminic acid	$C_{15}H_{28}O_2$
Hypoparic acid	$C_{16}H_{30}O_2$
Oleic acid	$C_{18}H_{34}O_2$
Doëglic acid	$C_{19}H_{36}O_2$
Erucic acid	$C_{22}H_{42}O_2$

The most important of these acids are stearic acid, fusible at 69.2° under a reduced pressure, and volatile in superheated steam without decomposition; it is readily soluble in alcohol and ether, and insoluble in water. Palmitic acid melts at 62°. Chevreul's margaric acid is a mixture of 10 parts stearic acid and 90 parts palmitic acid. Oleic acid is a colourless oily liquid which congeals at 4° and melts again at 44°. Nitrous acid converts it into its isomere, elaïdic acid, which melts at 44°.

Most fats consist chiefly of tripalmitine, tristearine and trioleine. Tripalmitine, generally called simply palmitine, melts at 60° and congeals at 46°; it is the chief constituent of palm-oil. Tristearine (stearine) $C_3H_5(C_{18}H_{35}O_2)_3$ melts at 63°, and if heated to 65° it solidifies at 61° and melts at 66°; if it is superheated for a length of time its melting-point sinks to 35°. Trioleine (oleine), the chief constituent of the liquid fats, solidifies at −5°, and is converted by nitrous acid into elaïdine fusible at 36°. If heated with water under a high pressure the triglycerides are split up into glycerine and fatty acid:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3H_2O = C_3H_5(OH)_3 + 3H.C_{18}H_{35}O_2.$$

The chief animal fats are, with the exception of butter, suets (beef and mutton) and hog's lard. Tallow is obtained by rendering (*i.e.*, melting out) the fat which collects in the intestinal cavity of oxen or sheep. The hardness of tallow depends on the species of animal from which it is obtained, and on the food which it has consumed. Dry fodder produces the hardest tallow, while the softest is obtained from animals fed on the waste grain from breweries and distilleries. Russian tallow is far harder than the German quality, since in Russia cattle subsist on dry fodder for more than eight months in the year. Tallow generally melts at 35°–37°. It contains 75 per cent. hard fat (tristearine and tripalmitine), the remainder is trioleine.

Goose-grease, which is a valued food-fat in Germany, is—or was—chiefly burnt in lamps in Russia. In Britain it is of little importance.

Fish-oil, seal-oil, obtained from the blubber of several varieties of Mammalia inhabiting the seas, especially of the colder regions of the globe, and belonging to the Cetacea and Phocena, varies somewhat in its properties, according to the mode of preparation and the animal from which it has been derived. The specific gravity of this oil is 0·927 at 20°; when cooled to 0° it deposits solid fat; it is readily soluble in alcohol, and consists of oleine, stearine, and small quantities of the glycerides of valerianic and similar fatty acids. Fish-oil, besides being an important material in soap-making, is also used in tanning, tawing, and leather-dressing operations.

Vegetable fats either become rancid on exposure to the air, and acid from the formation of free fatty acid, though they do not solidify, the *non-drying oils;* or they are converted into a solid mass by taking up oxygen, *drying oils.*

The most important non-drying oils from a technical point of view are :—Palm-oil, of vegetable origin, met with in the fruit of a palm-tree, *Avoira elais* or *Elais guinensis;* according to others, however, this oil is derived from the *Cocos butyracea, C. nucifera,* and *Areca oleracea,* trees growing wild, and also cultivated in Guinea and Guiana. The colour of this oil is a red-yellow, its consistency that of butter, while it possesses a strong but by no means disagreeable odour, similar somewhat to that of orris root. When fresh, this oil melts at 27°, but by becoming rancid as it is termed—that is, by its decomposition into glycerine and free fatty acids—its melting point rises to 31° and even to 36°. It is chiefly composed of palmitine mixed with a small quantity of oleine. Palmitine, formerly confused with margarine, is saponified by the alkalies and converted into potassium or sodium palmitate, while glycerine is set free :—

$$\left.\begin{array}{l}\text{Palmitine (tripalmitine), } \left.\begin{matrix}C_3H_5,\\(C_{16}H_{31}O)_3\end{matrix}\right\}O_3\\ \text{Potassium hydroxide, } 3KOH\\ \quad\text{(caustic potassa)}\end{array}\right\} = \left\{\begin{array}{l}\text{Glycerine, } \left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3,\\ \text{Potassium palmitate, } 3\left\{\begin{matrix}C_{16}H_{31}O\\K\end{matrix}\right\}O.\end{array}\right.$$

Palmitic acid is very similar to, and has often been confused with, stearic acid; the former is in a pure state a solid white crystalline mass, which fuses at 62°. Palm-oil often contains one-third of its weight of this acid in free state, and the quantity increases with the age of the oil. The red-yellow pigment of the palm-oil not being destroyed by its saponification, the soap made from this oil is of yellow colour, but if, previous to saponification, the oil is submitted to a bleaching process, that is to say, the pigment destroyed by chemical agents, such as the joint action of potassium bichromate and sulphuric acid, the oil becomes nearly white, and yields, on being saponified, a white soap.

Palm-oil has latterly come into use in the so-called white baths in turkey-red dyeing—[EDITOR]. Sometimes a cask of palm-oil arrives in England without having become rancid. Could this result be regularly secured palm-oil would doubtless supersede "margarine."

The illipe, or bassia-oil, very similar to palm-oil, is obtained by pressure from the seeds of the *Bassia latifolia,* a tree growing on the slopes of the Himalaya. At first the colour of this oil is yellow, but by exposure to sunlight it becomes white. Its

odour is not very strong, but rather pleasant. At the ordinary temperature of the air this oil has the consistency of butter; its sp. gr. is = 0·958; its melting-point from 27° to 30°. It is somewhat soluble in alcohol, readily in ether, and easily saponified by potassa and soda. In its saponification, oleic acid and two solid acids with a variable melting-point are formed. The galam butter produced by the *Bassia butyracea*, a tree met with in the interior of Africa, is sometimes confounded with palm-oil, to which it is very similar, but of a deeper red colour. Galam butter fuses at 20° or 21°, and is in its properties very much like palm-oil. Carapa oil and vateria tallow belong to the same class of fatty substances; the first, the product of the kernel of a species of *Persoonia*, a palm-tree met with in Bengal and Coromandel, is a bright yellow-coloured material, which at 18° separates into an oil and a solid fat, known as pine-tallow, Malabar tallow, and obtained from the fruits of the *Vateria indica*, is a white-yellow wax-like tallow, melting at 35°. Mafurra tallow is obtained by boiling in water the seeds or kernels of the mafurra tree found in Mozambique; this seed, very rarely seen in Europe, is of the size of small cacao beans. Mafurra seed also occurs in Madagascar and Isle de Réunion. The fat obtained from this seed has a yellow colour, the smell of cacao butter, and melts more readily than tallow. The fat of the seeds of the *Brindonia indica*, employed at Goa, instead of butter, also for medicinal purposes, and for use in lamps, is nearly white, melts at 40°, and is insoluble in cold, but somewhat soluble in boiling alcohol. Cocoa-nut oil, obtained from the kernels of the cocoa-nut (*Cocos nucifera*, *C. butyracea*), is largely used in the tropics, where the tree abounds. This oil is imported into Europe, and is also obtained here by pressing and by treating the kernels of the imported nuts with carbon disulphide. It is white, has the consistency of lard, but possesses a disagreeable odour and a somewhat foliated texture; its melting-point is 22°. Chemically considered this fat consists of a peculiar substance termed cocinin, with small quantities of oleine; by saponification the former yields glycerine and cocinic acid (cocoa-stearic acid), $C_{13}H_{26}O_2$. W. Wicke obtained in 1860, 61·57 per cent of fat from the kernels. During the last twenty years cocoa-nut oil has been largely used for soap-boiling, because it is an excellent material for the preparation of so-called filling soaps.*

Olive oil is obtained from the fruit of the olive tree, *Olea europea*, belonging to the natural order of the *Jasmineæ*, and largely cultivated in the whole of Southern Europe and the coastlands of North Africa.

In order to obtain an oil of good quality it is essential that the olives should be gathered when they are fully ripe, which happens in the months of November and December. Unripe olives yield an oil having a harsh bitter taste, while, again, over-ripe fruit yields a thick oil, readily becoming rancid. The method of oil extraction from olives as carried on in Southern France is the following:—The ripe olives are first reduced to pulp in a mill; this pulp is put into sacks made of strong canvas, or, better, of horsehair, and submitted to pressure. The first portion of oil thus obtained is the best and is known as virgin oil, or *huile vierge*. In order to eliminate all the oil as much as possible, the cake, after the first pressing, is treated with boiling water and again pressed. The oil thus obtained possesses a fine yellow colour, but is more liable to become rancid than the virgin oil. Notwithstanding the second pressure the cake retains enough oil to make it worth while to submit it to further operation. Some kinds of olive oil obtained by the second pressing are employed, under the name of Gallipoli oil, in dyeing Turkey-red. This oil has an acid reaction consequent upon its containing free fatty acids, is turbid, rancid, and possessed of the property of forming with carbonates of alkalies a kind of emulsion, which in dyeing is known as the white

* Cocoa-nut oil has recently been used for preparing an artificial butter which approaches cow-butter more closely than any other substitute. The rancidity and offensive odour are removed by treatment with alcohol and filtration over bone-black.—[EDITOR.]

bath. The olive oil used for the purpose of greasing wool in spinning is known as lampant oil. Under the name of *Huile d'enfer* is understood the olive oil deposited in the tanks where the water used for adding to the olives about to be pressed is kept; it is used in the manufacture of soap. During the last few years it has become the custom to exhaust the olives with carbon disulphide instead of pressing them.

Rape-oil and Colza-oil (formerly much used for burning in lamps) are obtained from the seeds of various kinds of *Brassica*, which are, in fact, merely varieties of *Brassica campestris*. The oils differ very little.

Beech oil, from the seeds of the beech (*Fagus sylvatica*), is used for food.

Sesame oil is obtained in India, Brazil, Greece, &c., from the seeds of *Sesamum orientale* and *S. indicum*. It much resembles olive oil, and is used for the sophistication of the latter.

Earth-nut oil is obtained from *Arachis hypogæa* in India and South America and much resembles oil of sesame.

The chief drying oils are:—Hemp-oil, obtained from the hemp-seed (*Cannabis sativa*), containing about 25 per cent. of oil, chiefly used for making black, green, or soft soap. When fresh pressed, hemp-oil possesses a bright green colour, which in time becomes a brown-yellow.* Linseed oil, like the former a so-called drying oil, is obtained from the well-known linseed (*Linum usitatissimum*), containing about 22 per cent. of this oil, the sp. gr. of which is at $12 = 0{\cdot}9395$. This oil consists chiefly of a peculiar glyceride which, on being saponified, yields a fatty acid different from oleic acid; moreover, linseed oil contains some palmitine.†

Nut oil, from the nuts of *Juglans regia*, and *poppy oil*, from the seeds of *Papaver somniferum*, are used in oil-painting and also as articles of food.

Cotton oil is now obtained in vast quantities from the seeds of the cotton shrub, and being a bye-product, formerly wasted, it is sold at a low price. It consists of 60 per cent. linoleic acid and 40 per cent. oleic acid. It is used as an article of food, either alone or in admixture with oleic acid. It appears to be perfectly wholesome.

The *Waxes*, with the exception of Japan wax, are not glycerides. The most important are—

Beeswax, collected by the honey-bee, *Apis mellifica*, and obtained by melting out the combs with warm water. It is yellow, seldom reddish, and may be bleached by exposure to air and light. Yellow wax melts at from 61° to 63°; bleached white wax at 70°. It is used for the production of tapers, candles, &c., and for smoothing thread, &c.

White wax is often adulterated with stearine, paraffine, or ozokerite. John first observed that wax is a mixture of these substances; the one, cerotic acid, $C_{27}H_{54}O_2$, is soluble in boiling alcohol; the other, myricine, is sparingly soluble in alcohol, and consists, according to Brodie, of the melissyl-ester of palmitic acid, $C_{46}H_{92}O_2 = C_{16}H_{31}(C_{30}H_{61})O_2$. The difference in the melting-point of different sorts of wax is due to the different proportions of the two constituents.

Chinese wax is now imported from China in quantity, and is derived from the wax plant-louse, *Coccus ceriferus*, which deposits it upon the trees—especially *Rhus succedanea*. It much resembles spermaceti in appearance, being snow-white, crystalline, brittle and fibrous, and fusible at 82°. On dry distillation it yields cerotic acid and cerotine, a body resembling paraffine. According to Brodie, Chinese wax is the ceryl-ester of cerotic acid, $C_{54}H_{108}O_2$, or $C_{27}H_{53}(C_{27}H_{55})O_2$.

Andaquies wax is produced by an insect found on the Orinoco and the Amazon. It melts at 77°, has the sp. gr. 0·917, and seems to have the same composition as beeswax.

* Hempseed oil contains 70 per cent. linoleic acid, 15 per cent. linolenic acid, and 15 per cent. oleic acid.—[EDITOR.]

† Linseed oil contains linolenic acid, isolinolenic acid and linoleic acid. Oleic acid is almost entirely absent.—[EDITOR.]

The chief vegetable waxes are:

Japan wax, from *Rhus vernicifera* and *R. succedanea*, is met with in commerce in round discs, soft and brittle; it melts at 42°; dissolves in boiling alcohol, and consists chiefly of tripalmitine.

Carnauba wax is imported from Rio de Janiero, and forms a coating on the leaves of a kind of palm-tree, *Copernicia cerifera*, or *Corypha cerifera*. It consists essentially of palmitic melissylester; it melts at from 82° to 83·5°, and on account of its high melting point it serves to make more fusible fats, as also paraffine and ceresine (mineral wax), fit for the manufacture of candles. Of late it has been used in the soap manufacture. Stuercke has isolated from it a hydrocarbon melting at 59°, three alcohols, and three acids, an alcohol $C_{26}H_{53}.CH_2OH$, melting at 76°, also myricyl alcohol $C_{29}H_{59}.CH_2OH$, melting at 85·5°, from which there was obtained melissic acid, $C_{29}H_{59}.COOH$, melting at 90°, and a bi-acid alcohol $C_{23}H_{45}(CH_2.OH)_2$, having a melting-point about 103·5°; from this alcohol there was obtained the acid $C_{23}H_{46}(CO_2H)_2$ melting at 102·5°. An acid, $C_{23}H_{47}.COOH$, melting at 72·5°, isomeric with lignoceric acid; then an acid, $C_{25}H_{53}.COOH$ melting at 79°, identical or isomeric with cerotic acid; lastly, an acid $C_{19}H_{39}.CH_2OH.COOH$, an oxy-acid or its lactone, $C_{19}H_{38}CH_2.O.CO$, melting at 103·5°; from this there was obtained the acid, $C_{19}H_{38}(COOH)_2$, melting at 90°.

Palm wax, from the bark of *Ceroxylon andicola*, a palm growing in the upper regions of the Andes, is obtained by scraping and boiling with water. It melts at from 83° to 86°, and is perhaps identical with Carnauba wax.

Myrtle Wax is obtained in some of the more southern American States on boiling the fruits of *Myristica cerifera* with water. It melts at 45°.

Ucuhuba Wax, obtained in the Brazilian province of Para from *Myristica surinamensis*, is olive-green, and melts at 40°. It is used for candles.

Lubricants.—The various substances used for lubricating machinery have the object of diminishing friction, so as to economise motive power and diminish the wear and tear of the parts which come in contact. Such mixtures must neither contain nor form any acid capable of corroding metals, nor must they thicken in the air as do the drying oils, linseed and hemp-seed oil.

The lubricants chiefly in use have been olive and rape oil, often mixed with mineral oils; also other vegetable and animal fats, sometimes with the addition of graphite, &c., also resin oils and paraffines. The heavier mineral oils are now more and more coming into use as lubricants.

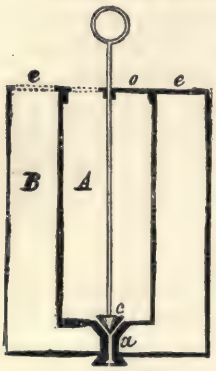
The American mineral oils used for this purpose are known as globe oil, Vulcan oil, topaz oil, star oil, &c. Valvoline is obtained from Hamburg; whilst in South Germany we more commonly meet with the thick-flowing Smaragd oil, dark brown, with a green fluorescence; opal, which is thin and yellow; and ruby oil, which is semi-solid at low temperatures. The Russian petroleum workings supply caucasine, &c.

A lubricant reduces friction merely by forming a layer between the moving surfaces and preventing their actual contact. The friction becomes less the more easily the molecules of the lubricant move upon each other. If the pressure is very strong, a highly fluid oil is driven out, and if the rotation is very rapid it may be thrown out centrifugally, so that the metallic surfaces come into immediate contact. Hence for strong pressures there is required a thick oil of little fluidity, and for light pressures a thin and very fluid oil. The oil must therefore be selected with due regard to the weight of the machinery, to its speed of rotation, and to the prevailing temperature. No one lubricating oil is equally well adapted for all purposes.

The examination of lubricants must include the detection and determination of any free acid, and the determination of the coëfficient of friction for different pressures and temperatures.

In order to ascertain the fluidity of an oil at different temperatures, the author uses the apparatus, Fig. 582. The outflow of the copper cylinder, *A*, consists of a fine platinum tube, 1·2 mm. in width and 5 mm. in length, enclosed in a thicker copper tube, *a*. The latter expands at its top like a funnel, and can be closed by the cone, *c*, the handle of which works up or down in a guide-frame, secured to the vessel. The inner vessel is connected by three slips of sheet-metal, *e*, to the external vessel, *B*, which rests on three feet, 11 centimetres high and not shown in the figure. In use, the vessel, *A*, is filled up to a mark with 65 c.c. of the oil in question, the vessel, *B*, is filled with cold or warm water, and the oil is stirred with a sensitive thermometer, until both it and the water outside are at the desired temperature. A bottle holding 50 c.c., with a narrow neck, is placed between the efflux opening, the stopper, *c*, is raised, and the time required for 50 c.c. to flow into the bottle is carefully noted. The end of the tube projecting out of the vessel, *B*, is expanded, whence its cylindrical portion, which determines the speed of flowing, has the same temperature as the liquid used for the experiment.

Fig. 582.



Varnishes.—By varnish we understand a liquid of an oily or resinous nature employed for coating various objects, the thin film becoming dry and hard, thus protecting the object on which it is laid from the action of air and water, and at the same time imparting a glossy and shining surface.

Linseed Oil Varnishes.—Oil varnishes are usually prepared from linseed oil, but sometimes, especially for artist's purposes, poppy seed and walnut oil (so-called drying oils) are used. Linseed oil (raw) becomes slowly converted by the action of the air into a tough, elastic, semi-transparent mass; but this property is possessed in a far higher degree by the so-called boiled oil—that is to say, an oil which has been brought by the action of heat and of oxidising materials into a state of greater activity, in fact, into a state of incipient slow oxidation, the result of which is the formation of the substance termed by Dr. G. J. Mulder* linoxine, which in many of its properties corresponds to caoutchouc. The drying of oil varnishes is not therefore due to evaporation (leaving, as is the case with alcohol varnishes, a coherent film of resin), but to the oxidising action of the oxygen of the air, whereby a coherent film of linoxine is formed. Linseed oil (raw) is converted into so-called boiled oil by boiling with litharge, zinc oxide, and manganese peroxide, which act upon the elaine, palmitine, and myristine of the linseed oil. The greater part of the linseed and other drying oils is linoleine, $3(C_{32}H_{27}O_3).C_6H_5O_3$, which by slow oxidation becomes linoxine $= C_{32}H_{27}O_{11}$, by the action of alkalies converted into linoxic acid, $HO.C_{32}O_{25}O_9$. It is certainly preferable to carry this operation into effect upon the water bath, or at least in vessels provided with steam jackets. The oxides are employed in coarse powders, which are suspended in a linen bag in the oil. In practice, 1 part of zinc oxide or litharge is taken to 16 parts of raw oil; and of the manganese 1 part to 10 of oil; the oxides become partially dissolved in the oil, while they aid in converting the palmitine, &c. (not linoleine), into plaster (lead or zinc soap). Boiled linseed oil usually contains from 2·5 to 3 per cent. of litharge dissolved. Neither the addition of zinc sulphate, nor such absurdly added substances as onions, bread crust, or beetroot, have any result whatever. Linseed oil intended to be mixed with zinc white should not be boiled with litharge, but with manganese peroxide. The lower the temperature at which linseed oil is boiled the brighter its colour. Mulder found that when raw linseed oil, especially if old, was kept for from

* This author published some years ago in the Dutch language a highly interesting and valuable work—practically as well as scientifically—on the drying oils.

twelve to eighteen hours at a temperature of 100°, it acquired the property of boiled oil. Sometimes, after boiling, linseed oil is bleached by exposing it in shallow trays 10 centimetres deep, best made of sheet lead, covered with sheets of glass, to the action of strong summer sunlight. Liebig's recipe for making a bright varnish is the following:—To 10 kilos. of raw linseed oil are added 300 grammes of finely pulverised litharge, after which there is added a solution of 600 grammes of lead acetate. The mixture is vigorously stirred, and, after the subsidence of the materials, the clear varnish is ready for use. Manganese borate is, according to Barruel and Jean, an excellent so-called siccative (dryer) when added to raw linseed oil, 1 part to 100 of oil. Mulder's experiments confirm this statement in every respect.

Varnish for Paper Hangings.—The varnish used for fixing gold or shearings of dyed wool upon paper-hangings, &c., is a solution of linseed oil and lead plaster in oil of turpentine. The mixture is obtained by first saponifying linseed oil with caustic alkali and precipitating the aqueous solution of this soap with a solution of lead acetate. The lead soap thus obtained is next dissolved in oil of turpentine.

Printing Ink.—This is, when genuine and when prepared from good linseed or walnut oil, anhydride of linoleic acid, $C_{32}H_{27}O_3$, mixed with very finely divided lamp-black, and obtained by heating raw linseed oil for several hours, at a high temperature (from 315° to 360°), whereby the fatty constituents—glycerine, palmitine, &c.—are volatilised. Usually the oil is heated in vessels directly exposed to the action of fire, and as the colour of the ink is black, a deep colour from the residue of the heating of the oil is not of much consequence. In order to render printing ink more rapidly drying, some manganese borate may be heated with it at 315° for some hours. The quantity of fine lamp-black (best re-ignited in close vessels, or exhausted with boiling alcohol) usually added to printing ink, amounts to about 16 per cent. Soap is necessary to be added in order to prevent smearing and assist in obtaining sharpness of impression. Coloured printing inks are obtained by adding to boiled oil red or blue or other pigments; for red, vermilion is used. The ink used in lithography and copper-plate printing is made thicker, a better black being added.

The varnish for lithographic ink has to be thicker than that for book-work. Copper-plate ink is a mixture of thick varnish with Frankfurt black. Instead of linseed or nut-oil, bankul-oil (from *Aleurites triloba*) has been proposed for the preparation of printing ink.

Fat Varnishes.—The so-called fat or oil varnishes are solutions of resins in boiled linseed oil mixed with oil of turpentine, benzol, or benzoline. Amber, copal, anime, gum dammar, and asphalte, are among the more ordinary resins employed for this purpose, the varnishes being made by melting, with the aid of gentle heat, the amber, copal, &c., to which, while liquid, boiling linseed oil is added. The cauldron in which this operation takes place should be only two-thirds filled; and the mixture of oil and resin kept boiling for ten minutes. The cauldron having been removed from the fire its contents are allowed to cool down to 140°, when the oil of turpentine is added. The quantities by weight are 10 parts copal or amber, 20 to 30 boiled linseed oil, 25 to 30 oil of turpentine. Black asphalte varnish is obtained in a similar manner by treating 3 parts of asphalte, 4 of boiled linseed oil, and 15 to 18 parts of oil of turpentine. Dark coloured amber varnish is not prepared from amber, but from the residue (*amber colophonium*) of the distillation of the empyreumatic oil of amber and succinic acid left in the still from the preparation of succinic acid. These varnishes are the most durable, but they dry slowly, and are more or less coloured.

Spirit Varnish.—The so-called spirit varnishes are solutions of certain resins—viz., sandarac, mastic, gumlac (shellac), anime in alcohol, aceton, wood spirit, benzoline, or carbon disulphide. Good spirit varnish ought to dry rapidly, give a glossy surface,

adhere strongly, and be neither brittle nor viscous. As shellac is frequently employed, the name of lac varnish is sometimes given to these varnishes. The spirit, usually methylated spirit, ought to be strong, about 92 per cent. The solution of the resins is promoted by the addition of one-third of their weight of coarsely powdered glass for the purpose of preventing the resinous matter caking together, and being thus to some extent withdrawn from the solvent action of the alcohol. In order to render the coating remaining from the evaporation of the spirit less brittle, Venice turpentine is usually added. Sandarac varnish is obtained by dissolving 10 parts of sandarac and 1 of Venice turpentine in 30 of spirit. Shellac varnish, more durable than the former, is obtained by dissolving 1 part of shellac in 3 to 5 of spirits. French polish is a solution of shellac in a large quantity of spirits, and when this polish is to be applied to white wood, the varnish is bleached by filtration over animal charcoal. Copal varnish, far superior to the foregoing, is made by first melting the resin at as gentle a heat as possible so as to prevent the coloration of the substance, which is next pulverised, mixed with sand, treated with strong alcohol on a water bath, and filtered. A solution of turpentine or elemi resin is added to render the varnish softer. Colourless copal varnish is obtained by pouring over 6 kilos. of previously pulverised and molten copal, contained in a vessel which may be closed, 6 kilos. of alcohol at 98 per cent., 4 kilos. of oil of turpentine, and 1 kilo. of ether; the vessel containing this mixture having been closed is gently heated. The solution is clarified by decantation.

Lacquers.—These are used chiefly for the purpose of coating instruments, and other objects of brass and coloured metallic alloys, so as to prevent the action of the atmosphere. Such varnishes are used for imparting a gold-colour to base metals; for this purpose alcoholic tinctures of gamboge and dragon's blood, or magenta, picric acid, Martius yellow, and coralline, are separately prepared and added, in quantities found by trial, to a varnish consisting of 2 parts of seed lac, 4 of sandarac, 4 of elemi, and 40 of alcohol.

Turpentine Oil Varnishes.—These are prepared in the same manner as the preceding. They dry more slowly, but are less brittle and more durable. Common turpentine oil varnish is obtained by dissolving ordinary resin in oil of turpentine; but this varnish is liable to crack. Copal is either dissolved in oil of turpentine without or after having been melted; in the latter case the varnish being coloured. When non-melted copal is used it is broken into small lumps, and is suspended in a stout canvas bag over the surface of the oil of turpentine contained in a glass flask, and placed on a sand bath, the vapours arising from the oil of turpentine gradually dissolving the copal. Dammar gum resin varnish, made with oil of turpentine, is prepared by drying the resin at a gentle heat and dissolving it in from three to four times its weight of oil of turpentine. This varnish, though colourless, is not very durable. Green turpentine oil varnish is prepared by dissolving sandarac or mastic in concentrated caustic potash solution, diluting with water, and precipitating with acetate of copper, the dried precipitate being dissolved in oil of turpentine.

Polishing the Dried Varnish.—In order to increase the gloss of varnished surfaces especially on metallic objects and coaches, carriages and woodwork in theatres, concert-rooms, halls, &c., the dry surface is first rubbed over with soft felt, on which some very fine pumice-powder is laid, and is next polished with very soft woollen tissue on which some oil and rotten-stone is placed, the oil being rubbed off with starch-powder. Instead of varnishes, solutions of collodion (fulminating cotton in alcohol and ether), and solutions of water-glass are sometimes used; while Puscher recommends a solution of shellac in ammonia, largely used by hatters.

Pettenkofer's Process for Restoring Pictures.—In order to remove the cracks often observed in old pictures, Von Pettenkofer has suggested exposure to the vapour of alcohol at the ordinary temperature of the air, the picture being placed in an air-tight

box, at the bottom of which is a tray containing alcohol. This method has been tried, but not only has it failed in many cases, but some pictures have been completely spoiled. According to Dr. G. J. Mulder's researches, the only effective preservative of pictures is complete exclusion of air. He suggests that pictures should be well varnished on the painted side as well as on the back, and next hermetically covered with well-fitting sheets of polished glass on the front, and some substance on the back impermeable to air. The real cause of the ultimate destruction of pictures as well as of paint is the gradual, but continuous, yet slow, oxidation of the linoxine, resulting in the crumbling to powder of the pulverulent matter—pigments—used as colours. It may not here be out of place to state that one of the best solvents of linoxine (dried paint) is a mixture of alcohol and chloroform, which may be advantageously used to remove stains of paint, and also of waggon and carriage grease from silk and woollen tissues.

Linseed oil varnish mixed with white lead, litharge, or red lead, or with a mixture of 10 parts litharge and 90 parts elutriated chalk is used for cementing articles of glass or porcelain. Instead of the chalk, there may be taken lime slacked to a powder, and instead of litharge zinc white.

As a cement for steam-pipes, &c., Stephenson uses a mixture of 2 parts litharge, 1 part lime slacked to a powder, and 1 part sand, the whole intimately mixed with hot linseed oil varnish. If alum soap (obtained by precipitating solution of alum with soda-soap) is dissolved in hot linseed oil, we obtain a mixture suitable for cementing stones. Common glaziers' putty is made by grinding up chalk with boiled linseed oil. If the oil has not been boiled it sets very slowly. Glycerine putty, a mixture of glycerine with litharge, is excellent for joining iron to iron, stone to stone, and iron to stone. The best proportions are 50 grammes litharge to 5 c.c. glycerine.

Iron putty consists of ferric oxide ground up with boiled linseed oil; it resists acids well.*

SOAP.

Soap, in the common acceptation of the word, is the product of the action of caustic alkalies upon fats, and consists essentially of potassium or sodium stearate, palmitate, or oleate. Though soap was known in the pre-historic ages, its manufacture was not properly conducted until Chevreul ascertained the nature of fats and the principles of saponification, and until the soda industry was developed.

The raw materials for soap are of two kinds, the natural fats or the fatty acids and the lye, an aqueous solution of caustic potash or soda.

The soap-boiler now rarely prepares caustic lye for his own use. He generally finds it more convenient to buy solid caustic soda and potash from the alkali manufacturers. Usually three different kinds of lye are prepared and kept, viz.: (1) Strong lye, 18 to 20 per cent. of alkali; (2) Middling strong lye, 8 to 10 per cent. of alkali; and (3) Weak lye, containing only 1 to 4 per cent. of alkali. This weak liquor is commonly used instead of water for lixiviating a new soda-ash and lime mixture. The sodium-aluminate obtained by the decomposition of cryolite is used in the United States under the name *Natrona refined saponifier*, for soap manufacturing purposes. Sodium sulphide may also be used instead of caustic alkali.

Theory of Saponification.—Before Chevreul published his researches, it was supposed that fats and oils possessed the property of combining with alkalies. Chevreul found, however, that fats separated from their state of combination as soaps possessed properties differing from those existing before they were saponified, the fact being that the substances we are acquainted with as oils or fats are compounds of peculiar acids, stearic, palmitic, margaric, oleic, all non-volatile substances; while certain fats which give off a peculiar odour contain, in addition to these acids, volatile fatty acids,

* On cements the reader may compare Spon's "Encyclopædia of Industrial Arts," pp. 623, *et seq.* —[EDITOR.]

as butyric, capric, capronic, valerianic, &c. The volatile acids in the ordinary oils and fats are combined with a sweet material, discovered by Scheele, and known under the name of glycerine.

According to Berthelot's researches, it is held that all the oils and fats which are used in soap-making are ethers of glycerine, $C_3H_8O_3$, that substance being viewed as a trivalent alcohol, $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$. Palmitine, for instance, the main constituent of palm-oil, is glyceryl-tripalmitate, or tripalmitine, that is to say, glycerine in which three atoms of hydrogen are replaced by the radical of palmitic acid, $\left.\begin{matrix}C_3H_5\\3C_{16}H_{31}O\end{matrix}\right\}O_3$. Stearine (tristearine) and oleine (trioleine) have an analogous constitution. When the fats, take palm-oil for instance, are saponified with caustic alkalies, say caustic soda, the fat—that is, in chemical parlance, the ether—is decomposed into alcohol, *i.e.*, glycerine, and soda palmitate, *i.e.*, soap, according to the following equation:—

$$\left.\begin{matrix}\text{Tripalmitine } \left\{\begin{matrix}C_3H_5\\3C_{16}H_{31}O\end{matrix}\right\}O_3\\ \text{and caustic soda, } 3NaOH,\end{matrix}\right\} \text{yield} \left\{\begin{matrix}\text{Glycerine, } \left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3,\\ \text{and soap, or sodium palmitate, } 3\left\{\begin{matrix}C_{16}H_{32}O\\Na\end{matrix}\right\}O.\end{matrix}\right.$$

The glycerine formed during the process of saponification remains, after the separation of the soap, dissolved in the mother liquor from which it is prepared. It is clear that such fats as palm- and cocoa-nut oil, which in their ordinary state contain fatty acids, are more readily saponified than the perfectly neutral fats, viz., olive-oil and tallow; while the oleic acid derived from the stearine candle manufactories is readily saponified by carbonated alkalies. This operation applies to colophonium (resin), which consists essentially of a peculiar acid, pinic acid, but in these instances no real saponification takes place, inasmuch as no glycerine is formed. The decomposition of a fat by an alkali does not take place suddenly and throughout the whole of the fat at once, in the manner of inorganic salts, but passes through several stages, the first being the formation of an emulsion of lye and fat; next fat acids and fat acid salts are formed, retaining the rest of the fatty matter in suspension; gradually the free fatty matter is saponified, and the fat acid salts are converted into neutral salts, or, in other words, soap.

When caustic potassa is used, soft soaps are produced, while the hard soaps result from the use of caustic soda. We distinguish soaps—

(α) As hard soaps or soda soaps;

(β) As soft soaps or potassa soaps.

According to the fatty substances used in soap-boiling, soaps are distinguished as tallow, oil, palm-oil, oleic acid, cocoa-nut, fish-oil, and resin soaps, &c. Technically, hard soaps may be divided into:—

(1) Grain soap;

(2) Smooth soap;

(3) Filled soap.

(1) Grain soap takes its name from the fact that the finished soap when being salted out from solution separates from the spent lye in the state of semi-solid, rounded lumps or grains, which solidify to a uniform mass free from bubbles. It is the only pure soap, being freed by the salting out from glycerine, superfluous lye, excess of water, or other impurities. The majority of soap-boilers no longer make this kind.

(2) Smooth soap is made by what is called polishing the grain soap. If such soap is boiled in the pan with water or weak lye it takes up a proportion of water, and loses the power of marbling. It is distinguished from grain soap merely by its larger proportion of water.

(3) Filled soaps are now unfortunately the commonest. They are so imperfectly

salted out that the entire contents of the pan remain together and are sold as soap. On cooling, the whole solidifies, and does not betray its proportion of water.

This property of appearing dry and hard, along with a heavy percentage of water, is a peculiarity of cocoa-nut oil soaps, which communicate the same property to tallow and palm-oil soaps. A yield of 200 to 300 kilos. soap from 100 kilos. fat is nothing uncommon, especially if water-glass is used.

The mixture of oil 100 kilos., resin 70 to 80 kilos., water-glass 300 kilos., talc 100 to 150 kilos., and soda-lye at 56° Tw. 240 kilos., gives a yield of 800 kilos. of a product which sells as soap.

Chief Varieties of Soap.—The German tallow soap or curd soap is essentially a mixture of sodium stearate and palmitate, and it is commonly prepared indirectly by first saponifying tallow with caustic potassa, and next converting, by means of common salt, the potassium stearate and palmitate into the corresponding sodium compound.

The soap-boiling pan employed is somewhat conical in shape. It is made of cast-iron, and provided at the top with a high lintel or bulwark to prevent any fluid boiling over. Supposing it to be intended to convert 10 cwts. of tallow into soap: Into the cauldron is first poured about 500 litres of strong lye at 20 per cent. (= 1·226 sp. gr.); next the tallow is added, and a wooden or iron lid having been fitted to the cauldron, the fire is kindled. When ebullition sets in, it is kept up, with occasional stirring of the contents of the cauldron, for five consecutive hours. The materials in the cauldron are converted into soap-glue, as it is termed, a gelatinous mass, which, if the operation has been well conducted, ought not, upon the addition of fresh lye, to become thin, while it also should not flow in drops, but similarly to treacle from a spatula. The production of this substance is promoted by adding oil of tallow to the lye gradually and in small portions at a time.

Mège-Mouriès recommends either yolks of eggs, bile,* or albuminous compounds. As proved by the researches of F. Knapp, it is always advantageous to first convert the fat, with the requisite quantity of lye, into an emulsion, and to leave the lye either not heated at all or only to 50° in contact with the fat, so as to saponify first slowly in the cold and to finish off with ebullition. When caustic soda-lye is used it is of a density of from 14° to 17° Tw. (= 1·072 to 1·088 sp. gr.). When the saponification is complete the operation of fitting or parting is proceeded with, and consists in adding from 12 to 16 lbs. of salt to 100 of tallow. The soap is kept boiling until the soap-glue has become a greyish mass, from which the mother liquor or under-lye readily separates, the latter being let off by a tap; or, if no tap is fitted to the cauldron, the soap is gradually ladled over into the cooling tank. The addition of salt not only aims at the separation of the soap from the lye, but also at the partial conversion of the potassa into soda-soap. If the soap-glue has been removed, it is again put into the cauldron, and there is added a moderately strong lye, and heat again applied. The soap again becomes quite fluid, but consists chiefly of soda-soap glue. The ebullition is kept up, and during its continuance fresh lye and salt are added alternately. By continued boiling the soapy mass becomes more and more concentrated; as soon as the foaming ceases, and the whole mass is in a steady ebullition, it is again ladled over into the cooling-tank, or the mother liquor is tapped off. The object to be gained by this second boiling is the conversion of the material into a uniform mass free from air-bubbles; this object is promoted by beating with iron rods. The hot soap is next placed in a wooden box, so constructed that it can be taken to pieces; upon the bottom of this box, which is perforated, a piece of cloth is stretched, so as to allow of any adhering lye running off. When the soap is cool the box is taken to pieces, the soap cut into bars, and

* Ox-gall is the finest soap known for cleansing dyed goods, especially silks. Its synthetic production without the unpleasant smell would be a most valuable invention.—[EDITOR.]

these are placed in a cool, dry room. The cutting of the soap into bars is now effected by machinery; formerly it was performed by hand with a peculiar tool, a copper-wire with suitable handles, such as cheesemongers sometimes use. 10 cwts. of tallow yield on an average 16⅝ cwts. of soap, which by drying loses some 10 per cent. As it is impossible, even with repeated applications of salt, to convert potassa-soap completely into soda-soap, the German curd-soap, or *Kernseife*, is always mixed with a considerable quantity of potassa-soap, to which it owes its peculiar softness. According to the researches of Dr. A. C. Oudemans (1869), only half the potassa is converted into soda-soap.

Olive Oil Soap.—This kind of soap, also known as Marseilles, Venetian, or Castilian soap, is chiefly prepared in the southern parts of Europe. The olive oil is frequently mixed with other kinds of oil, such as linseed, poppy seed, cotton-seed oil, &c. Two kinds of lye are employed in the preparation of this soap; the first lye is only a caustic soda solution, and used for fitting or preparatory boiling; the other lye is mixed with common salt, and intended to effect the separation of the soap. The preparatory boiling aims at the formation of an emulsion or the production of an *état globulaire*, whereby the contact of oil and alkali is greatly promoted, and a real soap-glue ultimately results. In order to remove the water from this material as much as possible, a lye containing common salt is employed, and lastly by a third boiling the saponification is rendered complete. By the use of the lye containing common salt it is possible to keep the soap-glue in such a condition that it can take up alkali without combining with the water. The preparatory boiling, or fitting, is carried on in large copper vessels, capable of containing 250 cwts., the caustic soda employed for this purpose having a strength of from 8·2° to 12·5° Tw.(= 1·041 to 1·064 sp. gr.). The lye is brought to ebullition first, and the oil to be saponified is next added, care being taken to stir the mixture in order to promote the reaction. Gradually the mass becomes thick, and as soon as black vapours arise, due to the decomposition of a small quantity of the soap-glue by coming in contact with the very hot copper, there is added the stronger lye of 30° Tw. (1·157 sp. gr.). If it is intended to produce a blue-white soap, some sulphate of iron is added. As soon as the mass has become sufficiently thick, the soda-lye, mixed with salt, is added. After some hours the soap entirely separates from the mother liquor, which is then run off, and fresh lye added, also containing common salt. The final boiling is then proceeded with, the lye having a strength of from 30° to 45° Tw. The ebullition is continued gently until the alkali is exhausted, when the mother liquor is again run off, and fresh lye mixed with common salt again added; this operation is repeated some four to six times, when the soap is at last quite ready. This stage is indicated by the absence of all smell of oil and the peculiar grain of the mass, which is left to cool; but if sulphate of iron has been added, it is necessary to stir the soap continuously until nearly cold, in order to produce the mottled appearance due to the formation of iron sulphide from the sulphate by the action of the sodium sulphide of the soda-lye. Mottled soap is produced in England by adding a concentrated solution of crude caustic soda, containing sodium sulphide, to the liquid soap, previously being impregnated with iron sulphate. When nearly cold the soap is placed in wooden boxes and left to completely solidify. After from ten to twelve days it is ready for being cut into bars. 64 litres of oil = 58 to 60 kilos., yield from 90 to 95 kilos. of soap. White-oil soap is prepared in a similar manner, but purer materials are employed. A good sample of Marseilles mottled soap should contain :—

	I.		II.
Fat acids	63	...	62
Alkali	13	...	11
Water	24	...	27
	100	...	100

Oleic Acid Soap is obtained from crude oleic acid, a bye-product of stearine candle manufacture. The oleic acid produced by the distillation process is less suitable for soap-making purposes. Oleic acid is saponified simply by being mixed with a strong solution of sodium carbonate, or by the application of caustic soda. In the use of the sodium carbonate, however, there is the disadvantage of the effervescence due to the evolution of carbonic acid, and consequent boiling over or spilling of the materials. Pitman uses the sodium carbonate in a dry state. Heat is best applied by Morfit's arrangement, in which steam is passed through a system of pipes moved by machinery and acting as stirrers. Resin is sometimes added. As soon as the mass has acquired sufficient consistency, and the effervescence ceases, the soap is put into moulds to cool and solidify. When caustic soda is used, half the lye (sp. gr. 1·15 to 1·20 = 30·4° to 40° Tw.) is first poured into the cauldron and brought to ebullition, next the oleic acid is added, and as soon as the soap-glue is formed, the other half of the lye is put in, and the ebullition continued until the soap is formed. The separation from the mother liquor is greatly promoted by the addition of some salt. The soap is poured into moulds to cool and solidify. In order to impart greater hardness to the soap, from 5 to 8 per cent. of tallow is added to the oleic acid. 100 kilos. of oleic acid yield from 150 to 160 kilos. of soap, which, when well made, consists of—

Fat acids	66
Soda	13
Water	21
	100

Resin-Tallow Soaps.—Colophonium and ordinary fir-tree resin combine at boiling heat more readily with alkalies than do fats and oils; but the compounds obtained by treating resin alone with alkalies are not soaps in a chemical sense, nor have they the appearance or properties of soap. When tallow is saponified along with a portion of resin, a true soap is obtained. In England resin-tallow soap is manufactured very largely by first preparing a tallow-soap, and when this is ready adding to it from 50 to 60 per cent. of the best resin, previously broken into small lumps. The mass is thoroughly stirred, and after the resin has been incorporated with the tallow, the mother liquor or under-lye is run off, and the soap-making finished by boiling with a quantity of fresh lye at from 10° to 13° Tw. The insoluble alumina and iron soaps having been removed as scum from the top of the liquid, the hot soap is poured into moulds made of wood or sheet-iron; sometimes palm-oil is added in order to improve the colour of the soap. Usually, palm oil is not saponified alone, but is added to tallow; by treating a mixture of 2 parts of tallow and 3 parts of palm oil with potassa or soda-lye in the ordinary manner, and by mixing this soap with a resin soap prepared from 1 part of resin and a proper quantity of potassa-lye, the German palm-oil soap is obtained.

Cocoa-nut Oil Soap.—The manufacture of cocoa-nut oil soap resembles that of the other kinds of soap. With a weak lye cocoa-nut oil does not form the emulsion common to other soaps, but swims on the surface as a clear fat; when, by boiling, the lye has reached a proper consistence, the oil suddenly saponifies. A strong soda-lye is used in the preparation of this kind of soap. Cocoa-nut oil in saponifying does not separate from the under-lye; therefore potash-lye is never employed. To prevent the separation of the soap from the mixing, the quantity of caustic-lye used must be accurately measured. Pure cocoa-nut oil soap hardens quickly. It is white, like alabaster, shiny, soft, and easily lathered; it has, however, a peculiarly unpleasant smell, which cannot be entirely masked by any perfume. Cocoa-nut oil is seldom used alone, but usually as an addition to palm oil and tallow. This kind of soap can be made without boiling, by merely heating it to 80°, by means of steam, to melt the fats, a strong soda-lye being added,

and the mixture quickly stirred. This is known as the "cold method," and soap can be thus prepared in large quantities in a short time, and is generally hard and dry. When exposed to the air for a month or so, the soap loses considerably in weight, and becomes effloresced superficially. B. Unger (1869) prepares a soap in the following manner: He saponifies palm-oil with soda-lye and salt as usual. The product is sodium palmitate. At the same time cocoa-nut oil is saponified by means of carbonated and caustic soda-lye; this is added to the palm-oil soap, and they are boiled. As a rule, there are taken 2 parts of palm-oil to 1 part of cocoa-nut oil; and to 100 parts of the latter are added 14·3 parts of caustic soda (Na_2O) and 12·8 parts of sodium carbonate. According to Unger's experiments, this soap contains 5 mols. sodium palmitate, 1 mol. sodium carbonate, and x mol. water. The "marbling" or "mottling" is effected in the following manner:—Colouring matters, oxide of iron, brown-red, Frankfort-black, are mixed with a small portion of soap; this is poured into the rest of the soap, with which it forms layers of unequal thickness. The entire mass is now stirred, and by this means a marbled or grained appearance imparted.

Soft-Soap.—As before mentioned, potash forms with fats and oils only a *soft*-soap, which does not dry when exposed to the air, but on the contrary absorbs water, remaining constantly like a jelly. As a rule, these so-called soaps are impure solutions of potassium oleate in an excess of potash-lye, mixed with the glycerine separated in the saponification. Soft-soaps can be prepared only with potash-lyes, although in practice 1 part of soda-lye is substituted for a part of the potash to assist in somewhat hardening the soap. There is no separation of the soap from the under-lye, which contains all the impurities; consequently these are disseminated in the soap.

In consequence of the solubility and cleansing properties of soft-soap, its use is preferred to that of soda-soap in the manufacture of cloth and woollen articles. It will have been seen that the difference in manufacturing hard- and soft-soaps consists in employing potash-lye for the latter, and soda for the former. Wood-ash is not used in preparing the potash-lye, but always pure potash; the preparation follows the usual method with caustic lime. The fats used are mixtures of the vegetable and animal oils, as the fish-oil known as "Southern," with rape, hemp, and linseed oils. The particular oil used varies according to the time of the year and market price: in winter the soft oils are employed; in summer the firmer oils. Soft-soap is generally used for fulling and scouring; but abroad it is sometimes used for washing linen, to which it imparts a most disagreeable fishy odour, hardly concealed by any amount of perfume. The best soft-soap is made from hemp-seed oil, this oil imparting a green tinge, which, however, can be imitated by adding indigo to inferior soaps. Summer soap, as it is termed, contains, owing to the fat employed, more potassium palmitate in proportion to oleate than the winter soap. Sometimes saponification is effected with a mixture of hemp- and palm-oil or tallow, of train oil and tallow, &c.

The boiling of the soft-soap commences with a strong lye containing from 8 to 10 per cent. potash, by which an emulsion is formed. The scum is dashed about with a stick, the beating-stick, and by this means all the alkali is taken up. A fresh lye is then added, and the boiling continued, until the soap upon cooling stiffens into a clear tough mass. When the soap contains too much caustic alkali, which can be ascertained by the taste, more oil is added. The *clear-boiling* now commences, during which the excess of water is removed. To avoid lengthy evaporation a concentrated lye is employed, and the soap, instead of bubbling up, has its surface covered with blisters as large as the hand; these blisters are termed leaves. When the boiling is finished—ascertained by placing some of the soap to cool on a glass plate, from which, if firm, it can be separated—the soap is cooled, and stored in barrels.

Soft-soap will take up a considerable quantity of water-glass solution without alteration. Recently, for fulling, there has been added to the soft-soap a solution of potassium sulphate, or a mixture of alum and common salt, and also potato starch.

Various other Soaps.—Another soap is prepared from hog's-lard, and when scented with oil of almonds or essence of mirbane (nitrobenzol) is sold as almond-soap, and as a cosmetic. A soap is made from the grease of sheep's-wool. The so-called bone-soap is nothing more than a mixture of the usual hard or cocoa-nut oil soap with the jelly from bones. The bones are first treated with muriatic acid to separate the calcium phosphate. A variety of bone-soap is the Liverpool common soap. Flint-soap is an oil- or tallow-soap with which siliceous earth is mixed. When powdered pumice-stone is substituted for the siliceous earth, the soap is called *pumice-soap*. In America as well as in England a water-glass solution is substituted for the siliceous earth, although according to Seeber the result is not so efficacious. Cocoa-nut oil soap, however, containing 24 per cent. of sodium silicate and 50 per cent. water, is very firm. In the United States water-glass is added to the soap when, still hot from the boiling-pan, it is poured into the moulds. The water-glass solution is of a density = 60° Tw. (= 1·31 sp. gr.); the proportion of soap is 60 per cent. This kind of water-glass soap generally sets hard. Recently cryolite and sodium aluminate have been employed.

Toilet-soaps.—On account of the reduction in the duty toilet soaps are now very largely in demand. They are generally made by re-melting and perfuming common soap. English toilet soap is considered the best, as that of France and Germany being perfumed while cold is not so uniform a product.

There are three modes of preparing toilet soap, viz.:—

(1) By re-melting raw soap;
(2) By the cold perfuming of odourless soap;
(3) By direct preparation.

(1) In the method of re-melting, good raw soap is scraped into a boiling-pan, and after melting and skimming the perfume is added. The soap is then cast in moulds of the required form. (2) In the method of perfuming in the cold, odourless soap is cut into fine shreds by a machine; the perfume is then added, and the soap is passed between rollers, the sheets or bars thus formed being cut into tablets. Struve, of Leipsic, has invented a machine by means of which soap is stamped into the shape required. (3) The direct preparation of toilet-soap consists in colouring and scenting pure white common soap without an intervening cooling. The colouring materials are—for red, cinnabar, coralline, and magenta; the violet tar-colours for violet; for blue, ultramarine; for brown, a solution of raw sugar or caramel. Windsor soap is prepared in the following manner:—40 lbs. of mutton tallow and from 15 to 20 lbs. of olive oil are mixed with soda-lye marking 19°, making a soap of 15°; finally, with lye marking 20°, when the soap is of the consistency of marrow. The excess of lye is then neutralised. When the soap is set it is allowed to stand from six to eight hours, and during this time most of the under-lye separates. It is then placed in a flat form, and pressed until no fluid exudes. It is scented with cumin oil, bergamot, oil of lavender, oil of thyme, &c. Rose soap, *savon à la rose*, is manufactured by melting the ingredients of three parts of oil-soap with two parts of tallow-soap and sometimes water; the perfume is attar of roses, oil of roses, or gilliflower water, the colouring-matter being generally cinnabar. Shaving-soap must not contain free alkalies. It is sometimes prepared by boiling fat acids with a mixture of potassium and sodium carbonates. Lather-soaps have in equal volume only half the substance of the other soaps. Palm- or olive-oil soap is melted with an addition of one-third to one-eighth the volume of water, and the mass stirred until it has increased to double the

volume. It is then placed in a mould. It should be remarked that the oil-soaps, and not tallow-soaps, are the true formatives of the lather-soaps.

Transparent Soap.—Ordinary dry tallow-soap is cut into splinters, and heated with an equal weight of alcohol, in which the soap dissolves. The mixture is allowed to cool; therewith all impurities are thrown down, and the clear fluid is placed in the moulds, where it has to remain from three to four weeks to harden. Tincture of cochineal and aniline red are employed for colouring transparent soaps, and also Martius's yellow. The perfume is chiefly oil of cinnamon, sometimes oil of thyme, oil of marjoram, and sassafras oil. Glycerine-soap is prepared from an alcoholic solution of ordinary soap, to which glycerine is added. Or 5 cwts. of soap with an equal quantity of glycerine are heated by steam in a copper vessel. The mixture is placed in moulds, and allowed to set in the usual manner. A solution of soap in an excess of glycerine (35 : 30) forms fluid glycerine-soap, which is of a clear honey consistency. Both varieties are perfumed with essential oils.

Uses of Soap.—Soap is used for cleansing purposes in washing, in bleaching cloth and woollen materials; for the preparation of lithographic inks, &c. The cleansing properties of soap are due to the alkalies it contains. The alkali, although combined with the fat acids, loses none of these properties, which are, in fact, included in the combination of the alkali with the fatty substances of the dirt to be removed. The explanation of the action chemically, according to Chevreul, is the following:—The neutral salts formed by the alkalies and the fat acids, stearates, palmitates, and oleates are decomposed by the water, whereby insoluble double fat acid salts are separated, while the alkali is set free. By means of the free alkali the impurities clinging to the materials are removed, and taken up by the fat acid salts, the suspended dirt being thus contained in the lather.*

Soap Tests.—The greater the quantity of fat acids combined in the soap, the higher is its value. A normal soap, besides alkaline fat acids, should only contain free water, the quantity of which gives a means of estimating the value of the soap. It is in the power of the soap-maker to manufacture 300 parts of a good hard soap out of 100 parts of fat. When too small a quantity of water is contained the soap becomes too hard, and much labour is lost in obtaining a lather. If, on the other hand, water is held in too large a quantity there is a great loss of material. The degree of hardness of the soap forms, therefore, another means of estimating its value. Many soaps contain 2 to 3 per cent. glycerine. But the proportion of water and the hardness of a soap are not the only means of estimation, there still remains the estimation of the neutral fat, acid, alkalies, the free alkali, common salt, or unsaponified fat in the residue left after the drying of the soap. According to W. Stein, the presence of free alkali may be ascertained by means of calomel, or according to Naschold, by mercurous nitrate. Uncombined fat retards the formation of a lather, and after a time imparts to the soap a rancid odour. But the worth of a soap can only be accurately ascertained by means of chemical analysis.

The table by Dr. Leeds (p. 919) gives a method for the examination of soaps.

Insoluble Soaps.—All soaps which have not a base of potassa or soda are insoluble in water. Calcium-soap plays an important part in the manufacture of stearine candles. It is obtained either by saponifying fat with calcium hydrate or by decomposing a soluble soap with a soluble salt of lime. It is constantly formed if we attempt to dissolve soap in hard water. Magnesium-soap is not readily formed in a direct manner, but it may be formed indirectly by dissolving common soap in sea water. Aluminium-soap is one of the most important of the insoluble soaps. Alumina does not saponify fats, but aluminium-soap is obtained by means of a sodium

* Soaps used for cleansing wool and woollen goods should always have a basis of potash, to the exclusion of soda.—[EDITOR.]

Weigh 5 grammes of the soap, and dry at 110°. The loss shows water. Treat residue with alcohol.

Solution contains uncombined fat, which, after the solvent has been evaporated at 110°, is dried and weighed.

Residue consists of soap and mineral constituents. Treat with alcohol.

Solution contains soap (fatty acids, resin, combined alkali), glycerine, and free alkali. Add two or three drops phenol-phthaleine, and titrate, if necessary, with normal sulphuric acid. The consumption of the latter represents free alkali, and is calculated as NaOH. Add water in large excess, expel alcohol by boiling, decompose with excess of normal sulphuric acid, boil, filter, and wash.

Filtrate contains the combined alkali and glycerine. The excess of sulphuric acid is titrated back with normal soda.

The rest of the sulphuric acid consumed represents the *combined alkali* which was present, and is calculated as Na_2O.

After titrating, evaporate to dryness on water-bath; treat with absolute alcohol on water bath, evaporate alcoholic solution in a tared capsule, dry, and weigh as *glycerine*.

Residue consists of *fatty acids* and *resin*. Dry at 110°, and weigh. Dissolve a part in 20 c.c. of strong alcohol, add phenol-phthaleine, and saponify with soda in slight excess. Boil, let cool, make up to 100 c.c. with ether, decompose with silver nitrate in fine powder, shake for ten minutes, and let settle.

Precipitate consists of silver stearate, palmitate, and oleate.

Solution contains silver resinate. 50 c.c. are filtered off, mixed with 20 c.c. HCl (1 : 2), the silver chloride is let settle, and an aliquot part of the ethereal solution is evaporated in a tared capsule. Dry at 110°, and weigh. The residue consists of *resinic acid*, accompanied by 0·00235 gramme oleic acid for every 10 c.c. of liquid evaporated. By deducting the resin from its joint weight with the fatty acids the weight of the latter is found.

Residue: Soda, salt, sodium sulphate, water-glass, and insoluble matter. Take up with 60 c.c. water.

Filtrate: Na_2CO_3, NaCl, Na_2SO_4, and water-glass. Divide into four equal parts.

Na_2CO_3. Titrate with normal sulphuric acid and calculate the Na_2CO_3.

NaCl. Titrate with normal silver solution, or weigh as silver chloride, and calculate as NaCl.

$NaSO_4$. Weigh as $BaSO_4$, and calculate as Na_2SO_4.

Water-Glass. Decompose with HCl; separate the silica, and determine, 1st, silica; 2nd, soda.

Residue. Starch and insoluble matter. Dry and weigh. Invert starch; determine sugar thus formed with Fehling's solution. Calculate into starch, and deduct its weight from total residue to find insoluble mineral matter.

or potassium aluminate. Jarry proposes to protect wood from moisture by saturation with aluminium oleate. Textile goods are often rendered waterproof by successive treatment with aluminium acetate and soap-lye, a process which results in the formation of an aluminous soap. In raising the colours of tissues mordanted with aluminium salts and afterwards dyed or printed with a solution of soap, there is formed aluminium oleate which is sometimes used as a size in the manufacture of paper. Lieber recommends aluminium palmitate.

Manganese-soap is obtained by decomposing manganese sulphate with common soap or by dissolving manganese carbonate in oleic acid. It is used as a siccative.

Zinc-soap, formed by double decomposition or by saponifying zinc oxide with olive oil with the aid of heat, is a yellowish-white mass. If obtained by the first method it quickly dries to a friable mass; if produced by the second method it has the consistence of a plaster. Zinc-soap is also formed when zinc white is used as an oil colour. Lead-soap may be formed by double decomposition or by saponifying litharge or white-lead with olive oil. It is a yellowish-white mass and is present in lead varnishes. Tin-soap formed by double decomposition is produced when tissues are raised by soaping after being mordanted with salts of tin. Copper-soap, obtained by double decomposition is a green, dry mass which becomes brittle. It is sparingly soluble in alcohol, more readily in ether or oils, and it can also be prepared by boiling copper carbonate in oleic acid. A mixed copper and iron soap, obtained by precipitating with soap a mixed solution of copper and iron, if ground up with litharge varnish and wax, serves to produce a permanent green bronze on plaster figures.

Mercury or quicksilver soap is prepared from mercuric chloride and soap; it is white, but turns grey on exposure to air and light. Silver, gold, and platinum soaps are severally prepared by double decomposition, but they are of little use. Gold soap is employed in gilding porcelain, and silver soap for darkening the hair.

Washing Powders, Extracts of Soap, Soap Powders, Washing Sugars, Soap Ash, Saponaceous, &c., are mixtures used both in manufactures and for domestic purposes. They vary greatly in their composition and their value. One of the commonest kinds is made by allowing soda crystals to melt in their own water of crystallisation, often with the addition of a small quantity of water to compensate for that which escapes during the process. Some palm oil, ground yellow resin, or ordinary soap, is incorporated with the mixture, and the whole is then poured out into large, shallow trays of sheet iron, in which it is diligently stirred during cooling, so that it solidifies not into crystals or coherent masses, but into a rough powder, having the appearance of coarse sugar. The supposed advantage of these preparations is that they dissolve more readily than soap and soda crystals. Some varieties are coloured with a little turmeric, and others with artificial ultramarine.

In the lower qualities, a considerable quantity of sodium sulphate (Glauber's salt) is melted down along with the soda crystals. It cannot be detected by the appearance of the sample.

Soap-pastes, or washing-pastes, consist of soda-lye with which farinaceous matter has been incorporated.—[EDITOR.]

Adulteration of Soaps.—In the manufacture of soap integrity is nearly beaten out of the market. The principal adulterant is water, which, by various artifices, is incorporated with the soap to an alarming extent. (See p. 913.) The other adulterants are silica, alumina, water-glass, or talc. Caustic alkali, though a necessary ingredient of the soap, becomes hurtful if present in excess, or if it has not been duly saponified. Unsaponified fats may also prove injurious in certain manufacturing processes.—[EDITOR.]

The reader may compare "The Art of Soap-making," by Alexander Watt. London: Crosby Lockwood & Son. "A Treatise on the Manufacture of Soap and Candles," by W. L. Carpenter.

London : C. & F. N. Spon. "Soap and Candles," by R. S. Cristiani, Philadelphia and London. "Manufacture of Soap," by H. Dussance, Philadelphia and London. "Soaps," by C. Morfit, New York.—[EDITOR.]

STEARINE AND GLYCERINE.

The preparation of the fatty acids can be effected by saponification with lime, with sulphuric acid, with water and high pressure, and with superheated steam and subsequent distillation.

Saponification with Caustic Lime.—The fat used is tallow (beef or mutton) or palm oil. Mutton tallow contains large quantities of solid fatty acids and is easier to work, but beef tallow is cheaper. The tallow imported from Russia is generally a mixture of beef and mutton tallow. Since palm-oil has been introduced in quantity and at a low price, it is used in many manufactories of stearine candles.

The fat is first melted in wooden vats lined with lead, the charge being 500 kilos. of tallow and 800 litres of water, heated by steam through a pipe, the end of which lies on the bottom, coiled in a spiral. After the fat is melted there are gradually added with constant stirring, 600 litres milk of lime, containing 70 kilos. of burnt lime (= 14 per cent. of the weight of the fat). After heating for from six to eight hours the formation of the lime-soap is completed. From the hard crumbly lime-soap the yellowish glycerine water (at 5·50° to 8·25° Tw.) is drawn off and worked up by concentration and distillation. According to theory, on the assumption that in neutral fats 1 mol. glycerine exists, combined with 3 mols. fatty acid, only 8·7 quick-lime should be required to 100 parts of fat. Still 14 per cent. were used at first, as it was found that an excess facilitates saponification, though it subsequently occasions a corresponding increase in the outlay for sulphuric acid.

Fig. 583.



The lime-soap is now decomposed by means of sulphuric acid, of which 137 kilos. are used to 500 kilos. fat and 70 kilos. lime. The sulphuric acid is diluted with water to 17° Tw. (containing in this state 30 per cent. H_2SO_4) placed in a decomposition-vat along with the lime-soap, heated by the introduction of steam and stirred for three hours. After the fatty acids are separated, the steam is shut off and the liquid is allowed to settle. The fatty acids collect on the surface and a great part of the calcium sulphate subsides to the bottom. The fatty acids are run off or skimmed off into a vat lined with lead, and in order to remove the residues of lime and gypsum they are washed first with dilute sulphuric acid of 1·089 sp. gr. under the action of steam and then with water. 500 kilos. tallow yield from 460 to 488 kilos. of fatty acids, or 74 per cent. The yield depends on the kind, the purity, and the treatment of the tallow. 100 parts of the fatty acids yielded from 43·3 to 48·4 parts of solid fatty acid, in the mean 45·9 part of a mixture of stearic and palmitic acid.

After the fatty acids have been freed as completely as possible from lime, gypsum, and sulphuric acid by repeated washings with water, they are kept for some time in a state of fusion to let the last traces of water escape. They are then allowed to congeal or crystallise, and the part which has not solidified—consisting chiefly of oleic acid—is pressed either in hydraulic presses or filter-presses, first in the cold and then in heat. The congelation is effected in moulds of tin plate, which, like chocolate moulds, are wider at the edge than at the bottom and hold about 2 kilos. of fatty acid.

The moulds are filled as follows:—The melted acids are conveyed by means of a

pump and the pipe, *B*, into a wooden funnel, *A*, which is placed over the entire length of a wooden scaffold on which the moulds are set above each other as shown in Fig. 583. Each mould has a spout at its upper edge; the fat then flows down through the spout into the next mould, and so on until all the moulds are filled. The supply is then cut off by closing the leaden spouts, *F*—through which the fat flows out of the funnel into the highest mould—by means of wooden plugs. The fatty acids are left in the moulds to crystallise slowly, which requires twelve hours in winter, but twenty-four in summer. The slower the crystallisation and the better the crystals are developed the more easily and completely the liquid portions may be removed by expression.

According to A. Kind the cooling should be effected slowly and as it may be required in order to obtain a well-crystallised mass. By sudden cooling there is obtained a mass from which the solid fatty acids can only be separated with difficulty. The cylinder used, *a* (Figs. 584 and 585), is turned smooth within; it is closed at both ends by the covers *b* and *c*, and is provided externally with ribs, *n*, set against each other which when the cylinder, *a*, is introduced into an exterior cylinder, *w*, coated with a non-conductive mass, join up to the corresponding ribs of the latter. There is thus formed a cooling-room serving for the admission of cold water and alternately

Fig. 584.

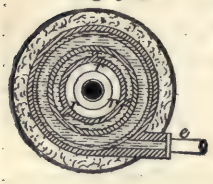
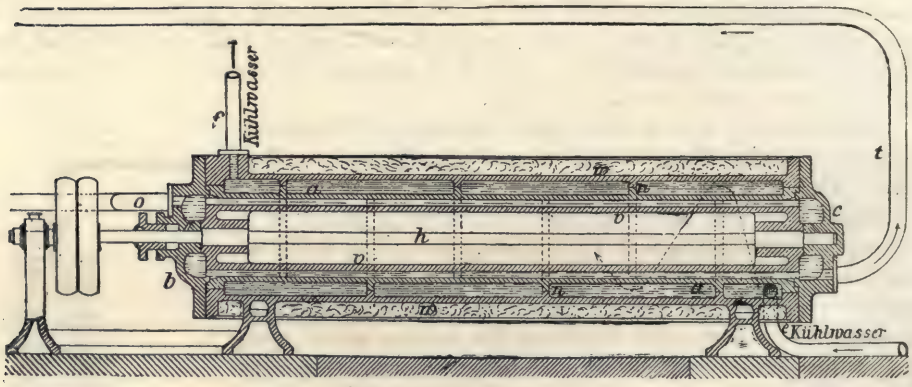


Fig. 585.



Explanation of Term.

Kühlwasser Water for refrigeration.

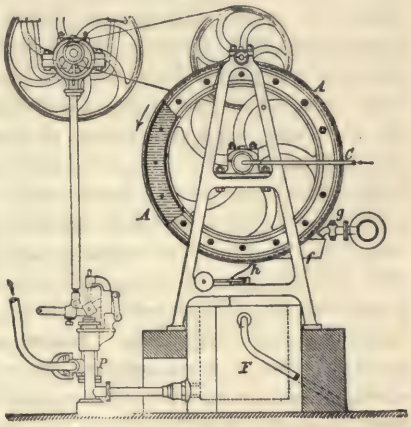
interrupted by partitions above and below, so that the cold water entering below at *e* is compelled to pass up and down round the cylinder in the direction of the arrow, finally leaving the apparatus of the pipe, *f*. For the oleine to be refrigerated there is in the cylinder, *a*, a narrow, annular space formed by the cylinder, *v*, placed concentrically to *a*, and set in slow movement with its axle, *h*. Around its circumference there are placed ribs which, as the axle revolves, brush slightly against the inside of the cylinder, *a*. These ribs may either be straight or have the form of a rapid screw thread. The oleine entering through the pipe, *o*, into the cover, *b*, is, on turning the axle, *h*, moved slowly in the opposite direction to the cooling water and is forced though the tube, *t*, to a store-tank.

Another apparatus for continuous working has been devised by Messener.

Petit uses a drum, *A* (Fig. 586), consisting of two cast-iron plates, which are held together by bolts and kept between two cylindrical sheet iron walls. Within the drum is cold water coming from a refrigerating machine which flows through the pipe, *C*, and a hollow arm, *D*, to the drum, and flows away through another arm. The drum

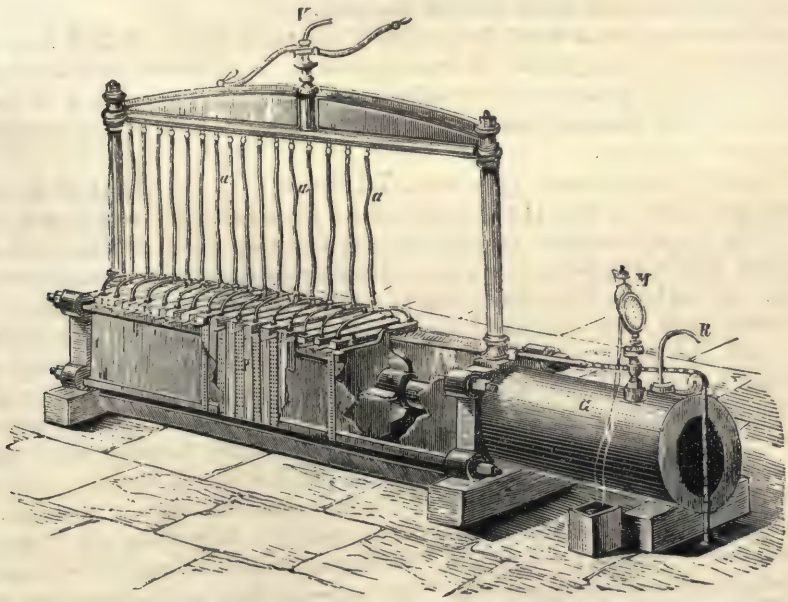
is moved by means of a circle of teeth from a shaft, *E*; this shaft drives a pump, *P*, by means of an eccentric. The pump sucks the congealed mass out of the receiver, *F*, and forces it to the filter-press. The external jacket of the drum as it revolves takes up a thin layer of liquid from the trough, *f*, to which the oleine flows through the cock, *g*; as the drum revolves this film of liquid congeals and is finally stripped off at *h* by a scraper, and falls into the recipient, *F*, which is also cooled by cold water. Hence the mass arrives at a Farinaux filter-press.

Fig. 585.



The separation of the solid and the liquid fatty acids is effected by cold pressing followed by hot pressing. For the former the moulds are thrown upon the press-cloth, a coarse, sack-like tissue of especially strong tough wool; the yellowish-brown cakes of fat are emptied into it, the press-sacks then filled are arranged between iron and zinc plates upon the table of a common hydraulic press and submitted to a pressure of 200,000 kilos. The oleic acid flowing off is received in collecting funnels placed below the table. It is used in the soap manufacture, for greasing wool, and recently as *oleic ether* mixed with clay forming an excellent oil for rendering leather supple. When the cold press no longer yields any oleic acid, hot pressing follows. Fig. 587 shows the

Fig. 587.



most important parts of a horizontal hot press, in which the press-bags and the intermediate plates are upright for the better escape of the oleic acid. The water used for pressing arrives through the pipe, *R*, into the press-cylinder, *C*, in which it acts upon the great piston, *T*, which presses the bags on the horizontal tables. The cakes of fat from the cold press are broken up, placed in horsehair bags (called in

French works *etreindilles*) and interstratified with the press-plates. These plates are of cast-iron and made hollow, so that they may be heated by the introduction of steam which arrives by the pipe, *V*, and the flexible tubes, *a*. In using the press the plates, *P*, and the sacks are arranged alternately and as soon as the table is full the steam-pipe, *V*, is opened to heat the plates. The access of steam is so regulated that the temperature first rises to 70°, then falls so low that it does not reach the melting-points of palmitic and stearic acid, but keeps the oleic acid liquid enough to flow off with ease. For this purpose a temperature of 40°, or even of 35°, is most suitable. At the same time the piston of the press is allowed to act. When oleic acid no longer flows off, the hard, solid fatty mass is taken out. It is contaminated with a little organic matter and ferric oxide only at the places where it has come in contact with the apparatus, and it is exposed to the light for some days. It is next, at some works, sorted into three or four qualities, according to its degree of purity. Besides the oleic acid obtained on hot pressing there crystallise out on cooling not inconsiderable quantities of palmitic acid, which is added in the next operation to the mixture of liquid and solid fatty acids. According to Girard there is sometimes placed over the press-cylinder, *C*, a manometer, *M*, connected with an electric signal apparatus which shows the workmen when the required pressure has been reached. Latterly the filter-press is coming more and more into use in the stearine industry.

The various sorts of solid, fatty acids obtained by hot pressure are next refined. To effect this the acids are melted by steam in very dilute sulphuric acid (4·75° Tw.) in washing becks lined with lead. This process is then repeated two or three times until all the sulphuric acid is washed away. It is then kept for some time in a state of fusion, to eliminate traces of water, and is finally poured into moulds. The washing water must be quite free from lime; if this is not the case the lime must be precipitated by oxalic or stearic acid. The fatty acid obtained is cast in tin moulds and supplied to candle-makers in the state of flat cakes.

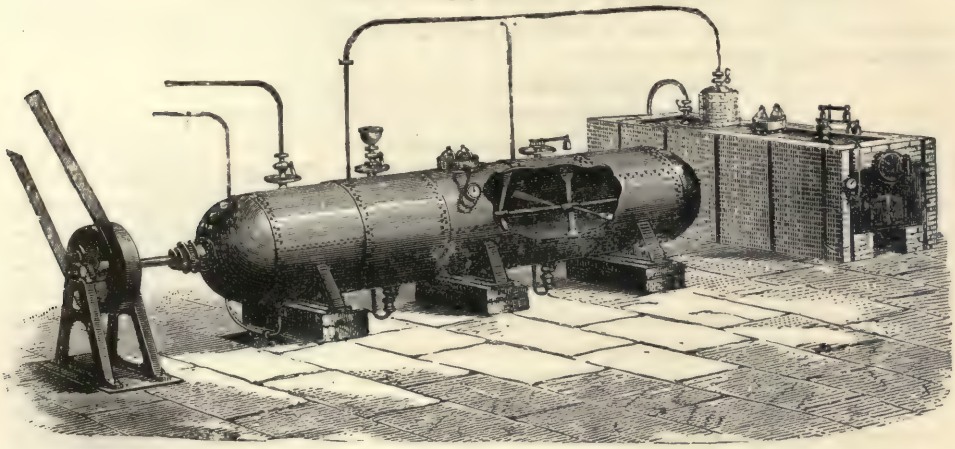
Saponification with a Reduced Proportion of Lime and the Use of High Pressure.—Milly observed that the quantity of lime required for saponification could be reduced from 14 per cent. of the weight of the tallow, not merely to 8, but to 4 or even to 2 per cent., if the mixture of lime water and fat is exposed to a higher temperature than has been customary.

He placed in a closed boiler 2300 kilos. of tallow and 20 hektolitres of lime milk, containing 50 kilos. of lime (2 per cent.), or 69 kilos. (= 3 per cent.), and caused steam of 182° (= a pressure of 10 atmospheres), to act upon the mixture so that the temperature within the boiler was 172°. After seven hours the saponification was complete. In the boiler there was a watery solution of glycerine and a mass of fatty acids, among which were distributed small quantities of lime-soap. The boiler was emptied and charged again, so that 6900 kilos. of tallow could be worked up in twenty-four hours. This procedure is advantageous, as the quantity of sulphuric acid required to decompose the lime-soap is much reduced. The Milly process is introduced in the great candle-works at Vienna, in the "Apollo candle-works" on the Schottenfelde in Vienna and Penzing, in Sarg's works at Liesing, and in those of Himmelbaur at Stockerau. Sarg, of Liesing, saponifies with 3 per cent. lime and a pressure of 10 atmospheres, obtaining 95 per cent. fatty acids, and 30 per cent. glycerine water at from 6·75 to 8·25° Tw. The fatty acids after cold and hot pressure yield 25 per cent. stearic acid and 35 per cent. "returns"—*i.e.*, fatty acids—which are pressed along with the total yield, which is finally 45 per cent. stearic acid and 50 per cent. oleic acid. The glycerine water is evaporated and after repeated distillation yields 5 to 6 per cent. glycerine.

The apparatus constructed by Léon Droux, fitted with an agitator for saponifying fats under pressure, deserves notice. (Fig. 588.) The cylinder is of copper, and is

generally 8 metres in length by 1·05 to 1·10 in diameter, the shaft fixed in the longitudinal axis of the cylinder is 50 mm. in diameter, and is fitted with copper arms for stirring; it revolves thirty times in the minute. For saponifying 3000 kilos. of fat there are used 80 kilos. of lime. The yield is 2800 kilos. fatty acids and 240 kilos. glycerine at 46° Tw. The increase of weight is due to the water taken up in the formation of glycerine. After the saponification is completed the contents of the boiler are run into a settling beck. The glycerine water obtained has the sp. gr. of 7° Tw. The decomposition of the lime-soap by sulphuric acid is made easier by its fluid state. The new apparatus has also been adopted in works where the distillation process is applied. In the latter the saponification with sulphuric acid is discarded and the fatty acid obtained is saponified in Droux's apparatus with slight acidification. Latterly its shape has been made globular instead of cylindrical. The axle of the agitator is horizontal; the apparatus is heated by direct steam distributer. Below, at the side of the apparatus are two trial-cocks, and above these is a man-hole for charging the apparatus. Each operation takes six or seven hours and the apparatus is kept for

Fig. 588.



five or six hours at a pressure of 7 or 8 atmospheres. When the process is at an end the contents of the tube are run off through a pipe opening into the apparatus below, by simply turning a cock. The product is then treated in the manner already described. The advantages of this new construction are said to be the greater strength of the globular vessels, the shortening the shaft and the decrease of condensation by surface cooling, as a globe has the largest capacity with the smallest surface.

In explaining this kind of saponification Payen holds that lime in its action upon tristearine, tripalmitine, and trioleine gives the impulse to a molecular movement which is completed by the water at a temperature of 172°. Pelouze had observed that lime-soap, obtained by precipitating an aqueous solution of calcium chloride with an aqueous solution of common soap with an equal quantity of water and then put in a digester with olive oil, saponifies the oil, at a temperature of from 155° to 165°, setting glycerine at liberty. From this and from other experiments he concluded that in Milly's saponification with a small percentage of lime, the process consists of several stages in which there is first formed a basic or neutral soap which is finally converted into an acid soap. But if we consider that Milly in his saponification with 2 per cent. of lime employs a temperature of 182° (corresponding to a pressure of 10 atmospheres), and that Wright and Fouché effected an almost complete decomposition of the fats at the same temperature with water alone and that Cloez effected a complete saponification of the fats at 200° with water, it seems simplest to assume that in this case water is the decomposing

element, and that the presence of 2 per cent. lime merely promotes and simplifies the saponification by cancelling a counter-affinity. The same result is attained still better by a small quantity of alkali.

Saponification by Means of Sulphuric Acid and Subsequent Distillation by Means of Steam.—It was known to Achard, in the year 1777, that the neutral fats are decomposed by concentrated sulphuric acid in a manner similar to the decomposition effected by caustic alkalies. This fact was again brought forward in 1821 by Caventon, and in 1824 by Chevreul, but was not scientifically investigated until 1836 by Frémy, and not industrially applied until the year 1841, when Dubrunfaut introduced the distillation of the fatty acids on the large scale. The crude fatty matter usually submitted to this process of saponification is of the kind that cannot be saponified by the lime process by reason of its impurities; thus, for instance, palm and cocoa-nut oil, bone and marrow fat, fat of slaughter-houses, kitchen-stuff, the products of the decomposition, by means of sulphuric acid, of the soap-water obtained from wool-spinning and cloth-making works, residues of the refining of fish and other oils, residues of tallow-melting, &c.

This process of saponification by means of sulphuric acid as carried on in the large establishment for stearine candle-making of Leroy and Durand, at Gentilly, near Paris, consists of three operations, viz.:—

(α) Saponification with sulphuric acid;
(β) Decomposition of the products of saponification;
(γ) Distillation of the fatty acids.

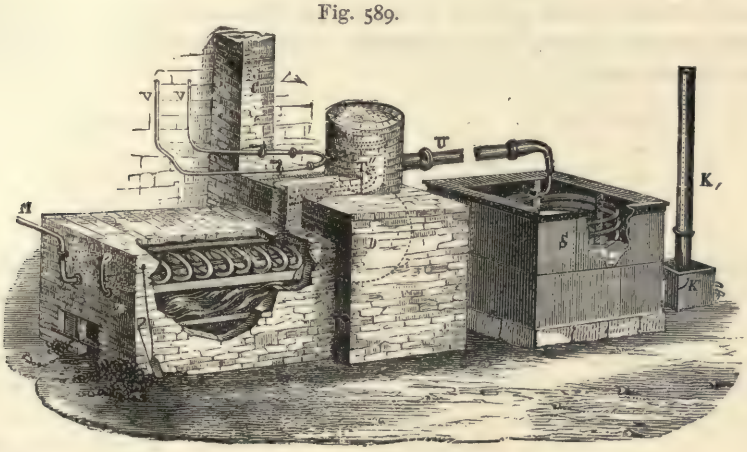
(α) In order to eliminate the greatest impurities first, the crude fatty matters are molten and kept in the liquid state for some time, so that the coarser impurities may subside. The fatty matters are then transferred to a kind of boiler made of iron boiler-plates lined inside with lead, and fitted with a stirring apparatus and a steam-jacket, connected by means of pipes with a steam-boiler, so that the apparatus may be heated. Into this vessel sulphuric acid at 153·4° Tw. = 1·8 sp. gr. is poured, the quantity of this fluid being regulated according to the nature of the fatty matters operated upon. Kitchen-stuff, fat from slaughter-houses, and the like require 12 per cent. of their weight of acid; palm oil requires from 6 to 9 per cent. according to quality. The fatty substances having been put into the vessel, the stirring apparatus is set in motion, and the steam turned on for the purpose of supplying heat to the vessel. The temperature to which the vessel is heated varies, being 177° in Price's Works, Battersea, while at Gentilly the heat is seldom higher than from 110° to 115°. During the operation the mass foams, becomes brown, and evolves sulphurous acid, partly due to the action of a portion of the concentrated sulphuric acid upon the glycerine, partly to its action upon the impurities present among the fatty matters. The neutral fat is converted into a mixture of sulpho-fatty acids and sulpho-glyceric acid. The saponification is complete after some fifteen to twenty hours' application of heat. According to De Milly's new process (1867) the tallow is heated to 120°, along with 6 per cent. of sulphuric acid, and the action of the latter is limited to two or three minutes; it is thereby possible to obtain 80 per cent. of the solid fatty acids in a condition at once fit for making candles without re-distillation, only 20 per cent. having to be distilled.

(β) Decomposition of the products of the sulphuric acid saponification. The mass is left to cool for three or four hours and is next transferred to large wooden tanks lined with lead, and previously one-third filled with water. At the bottom of these tanks steam pipes are fitted, by means of which the fluid contents of the vessel are soon heated to 100°. The sulphuric acid and the fatty acids are dissociated, and these bodies, partly combined with a larger quantity of hydrogen and oxygen than was present in the fatty acids from which they were formed, partly also in an unaltered condition, are found floating on the surface. After having been repeatedly triturated

with boiling water, the fatty acids are tapped or poured over into a vessel filled with water heated to from 40° to 50°, for the purpose of allowing the impurities to become deposited. The clarified fatty acids are next heated in a vessel placed on an open fire in order to evaporate all the water, after which they are submitted to distillation.

(γ) The distillation requires several precautions. Distillation with an open fire would convert the fatty acids into oil, gas-tar, and a carbonaceous residue, if the heat were sufficiently high. But when the temperature is properly regulated, the fatty acids are protected from the direct action of the fire. Air should be completely excluded from the distilling apparatus. With these precautions the fatty acids distil over without undergoing any essential alteration. These conditions are complied with by the use of superheated steam at a temperature of from 250° to 350°. The fatty acids are placed in a capacious retort with which there is connected on the one hand a pipe for admitting the superheated steam, and on the other an ordinary condenser. Fig. 589 shows

Fig. 589.



the arrangement of the distilling apparatus, the flame plays round the spiral coils and escapes through the chimney, *C*. The spiral begins at *M*, passes through the fire-box, comes out in front at *T'*, enters again at *T''*, and opens at last into the retort, *T'''*. The latter, which projects out of the fire is of copper or cast-iron; from the upper part of this retort there passes the tube, *U*, which is continued as an iron cooling-worm lying in an iron tank full of water. This pipe conveys the fatty acids into the receiver, *K*, whilst the gaseous products escape through the tube, K_1. When the apparatus is to be set in action, the spiral is first heated and the retort, *D*, is run three-quarters full of the melted fat through the pipe, *V*; steam is turned in at 300°. The air is then completely expelled and distillation soon begins in consequence of the high temperature, which does not fall below 200° in the retort. The fatty acids collecting in the receiver, *K*, are not identical at all times of the distillation.

When the several fatty acids are fractionally collected from the beginning to the end of the distillation their melting points are:—

	From Palm Oil.		From Kitchen-stuff and Bone Fat.
1st product	54·5°	...	44·0°
2nd „	52·0	...	41·0
3rd „	48·0	...	41·0
4th „	46·0	...	42·5
5th „	44·0	...	44·0
6th „	41·0	...	45·0
7th „	39·5	...	41·0

The water condensed with the fatty acids runs off from the receiver through a tap. At the beginning of the operation the water constitutes half the produce; towards the end only about one-third. With a retort capable of containing 1000 to 1100 kilos. of material the distillation takes some twelve hours. The end of the operation is indicated by the coming over of coloured products. There remains in the retort a black tarry matter the quantity of which amounts in the case of palm-oil distillation to from 2 to 5 per cent., and for kitchen-stuff to from 5 to 7 per cent. This residue is not removed after each distillation but left in the retort until it has accumulated to such an extent as to render its removal necessary. The first products of the distillation of palm oil saponified by means of fatty acids are so solid, that by pressure they do not yield any fluid acid, and are at once fit for the manufacture of candles. The products which come over afterwards are further purified by hydraulic pressure, re-melting, and washing with water. The substance obtained by pressure, more or less pure oleic acid, is only used for soap-making in this country, although abroad it is burnt in some kind of lamps. The oleic acid obtained by this process is essentially different from that obtained by the lime saponification process. The quantities of fatty acids obtained by this process of saponification are the following:—

From suint	47 to 55	per cent.
„ olive oil residues.	47 to 50	„
„ palm oil	75 to 80	„
„ fat from slaughter-houses . .	60 to 66	„
„ oleic acid	25 to 30	„

The boiler recommended by Julian and Blumsky for distilling fatty acids has two domes, *B* (Figs. 590 and 591), connected with corresponding coolers. The two end plates give exit to a number of tubes, *D*, connected by intermediate pieces. The steam which has been superheated in an especial arrangement enters through the pipe, *E*, passes through the tubes, *D* and *d*, and the two tubes, *e*, connected with the sieve-tubes, *n*, into the liquid. The mixture of fatty acids is filled in through the man-hole, *C*, to the height of the cock, *J*. The apparatus is then heated until drops appear at the cooling-tubes; the cock *F* is closed, *G* is opened, and superheated steam is allowed to enter through *E*. It passes through the pipe, *D*, and escapes at the cock, *G*. In this manner the entrance of steam-water into the boiler is avoided, which would interfere with the distillation. As soon as the temperature of the charge has risen so high that no more liquefaction takes place at *D*, and the steam in consequence escapes tolerably dry, the cock *F* is gradually opened to allow the dry steam to pass through the tube, *e*, to the sieve-tubes, *n*. The cock *G* is then closed and the distillation is continued by the double action of the superheater-tubes, *D*, and the sieve-tubes, *n*, until the distillate appears coloured, when the operation is stopped. Two hours after the distillation is at an end the residues may be let off through the cock *H* into a closed receiver; but if they are to be collected in an open cistern from five to six hours should elapse after the conclusion of the distillation.

Fig. 590.

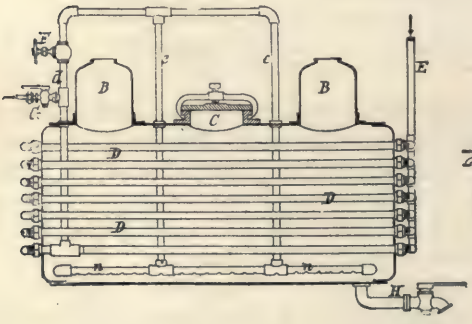
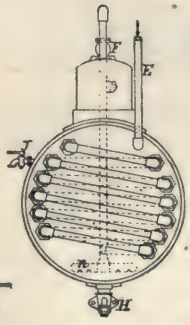


Fig. 591.



Zinc chloride, which in many respects (see p. 460) is similar in its action to sulphuric acid, has been proposed as a substitute for the latter. For countries into which sulphuric acid has to be imported zinc chloride might be of greater advantage, being capable of recovery and less dangerous and difficult in transport. When, according to the researches of L. Kraft and Tessié du Motay, a neutral fat is heated with anhydrous zinc chloride, a complete incorporation of these substances takes place between 150° and 200°; and by continuing the heating for some time, and washing the materials with warm water, or better with water acidulated with hydrochloric acid, there is obtained a fatty matter, which, on being submitted to distillation, yields the corresponding fatty acid, while only a small quantity of acroleine is formed. The zinc chloride, becoming soluble in the water used for washing, may be recovered by evaporating the fluid. The yield of fatty acids by this process is the same as that obtained by the use of sulphuric acid, while the fatty acids also agree as to their physical properties. The quantity of zinc chloride required amounts to from 8 to 12 per cent. of the fat.

Saponification with Water and High Pressure.—Some sixteen years ago another agent, capable of bringing about, in a manner similar to alkalies and acids, the dissociation of fatty matters into glycerine and fatty acids, was introduced, this agent being simply superheated steam at high pressure:—

$$\underbrace{3\left(\begin{matrix}C_3H_5\\C_{16}H_{31}O\end{matrix}\right\}O_3}_{\text{Tripalmitine.}} + \underbrace{3H_2O}_{\text{Water.}} = \underbrace{\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3}_{\text{Glycerine.}} + \underbrace{3\left\{\begin{matrix}H\\C_{16}H_{31}O\end{matrix}\right\}O}_{\text{Palmitic acid.}}$$

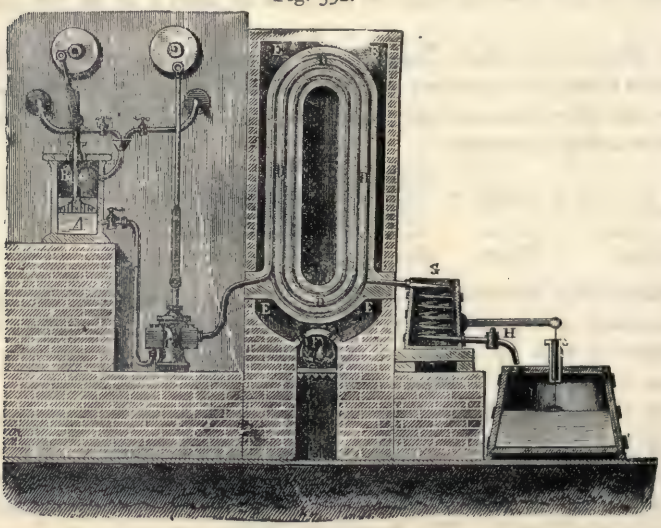
The idea of submitting fatty matters to a similar method of treatment is not a new one, for in the researches of Appert (1823) and Manicler (1826) some hints are given on the decomposition of fats by means of superheated water; but the aim of these technologists was different, for in their experiments they employed steam to separate the tallow from the cellular tissue it is contained in, and for that purpose a temperature of from 115° to 121° was quite sufficient, while at a temperature of 180° and a pressure of from 10 to 15 atmospheres (= 150 lbs. to 225 lbs. pressure to the square inch) water can exert a far more energetic action upon the neutral fats, dissociating them and thus setting free their constituents. The knowledge of this interesting fact is due to the researches of Tilghman and Berthelot, who almost simultaneously made this discovery in the year 1854, while shortly after Melsens, at Brussels, obtained the same result. As regards the industrial application of this discovery, Tilghman and Melsens made further researches; their modes of operating are very similar.

Tilghman adds to the neutral fat about to be decomposed one-third to one-half of its bulk of water, and pours this mixture into a sufficiently strong vessel in which the fluids can be submitted to the action of a temperature nearly as high as the melting-point of lead, 320°. This vessel is so arranged that during the operation it can be closed so as to prevent on the one hand the evaporation of water, and, on the other, admit of a sufficiently strong pressure. The process is carried on continuously by causing the fluids to circulate through a tube heated to the required temperature. Melsens uses a Papin's digester, in which the fat to be decomposed is heated to 180° to 200°, with from 10 to 20 per cent. water, to which from 1 to 10 per cent. of sulphuric acid has been added. Wright's and Fouché's apparatus consists of two hermetically closed copper vessels placed one above the other and connected together by means of two tubes, one of which reaches nearly to the bottom of the lower vessel, and ends in the upper one just above the bottom.

The apparatus of Tilghman, shown in section in Fig. 592, consists of a boiler, *A*, in which the fat—previously freed from impurities—is brought in contact with hot water, and is thus converted into a kind of emulsion. The piston, *B* perforated like a sieve,

which is moved quickly up and down in the vessel, *A*, effects an intimate mixture of the fat and the water. The forcing pump, *C*, drives the mixture through a long wrought-iron tube, *D*, which, as it appears in the figure, makes several bends in the furnace, *E*, and is heated by the fire, *F*, up to the melting point of lead. On issuing from the heating-tubes the mixture, the fat of which has been already split up into glycerine and fatty acids, passes through the worm, *G*, in which its temperature is reduced to 100°. It then escapes through *H* and falls into a suitable receiver. The valve placed at *H* is loaded in such a manner that when the heating-tubes have the proper temperature and the forcing-pump is not in action, it cannot be opened by the pressure within; consequently when the pump drives nothing into the apparatus, nothing can escape from it, if the temperature is not too high. When the forcing pump is at work and drives the mixture through the apparatus, the valve, *H*, opens and a corresponding quantity of the mixture escapes at *G*. The hot mixture of fatty acid and solution of glycerine is separated by settling, the fatty acid is washed with water, the solution of glycerine is concentrated and purified in the usual manner. A treatment for ten minutes is generally sufficient for the complete decomposition of the fats. A similar apparatus has been designed by Hugues.

Fig. 592.



The process of Melsens consists in treating the fat in a Papin digester at from 180° to 200°, with from 10 to 20 per cent. of water, to which from 1 to 10 per cent. of sulphuric acid has been added. The apparatus is a long horizontal boiler, in which the mixture of the water and the fat is effected in a small, second kettle, which is placed in connection with the former, filled with steam, which is then allowed to escape into the air, and the rest is condensed. The vacuum formed in the small boiler draws, on opening a cock, water and fat from the large, lower boiler. If a connection is then again effected between the upper parts of both boilers, the liquid mixture is violently forced into the lower boiler.

According to Marix the decomposition of fats by water can be effected at pressures of from 3 to 5 atmos., if a little magnesium carbonate and chalk are added.

Violette and Buisine have recourse to ammonia.

Manufacture of Fatty Acids by Means of Superheated Steam and Subsequent Distillation.—Allied to the process just described is the operation carried on by the well-known Price's Candle Company, Limited, at Battersea. Gay-Lussac and Dubrunfaut had already tried to apply to industrial purposes the fact that neutral fats are dissociated by distillation, yielding fatty acids; but notwithstanding that these *savants* employed steam, the results obtained did not answer the expectation, because a portion of the fatty matter was decomposed, yielding acroleine and leaving a carbonaceous residue. Wilson and Gwynne were more successful with their experi-

ments, and by using a distilling apparatus similar to that described on p. 503, they obtained by means of superheated steam the complete dissociation of the neutral fats into fatty acids and glycerine; while by closely watching and regulating the temperature, they could not only completely saponify the neutral fats, but also distil the fatty acids and glycerine over without undergoing any decomposition.

The retorts have a cubic capacity of 60 hectolitres, and are heated by direct fire to a temperature of from 290° to 315°. A malleable iron steam-pipe conveys steam at a temperature of 315° into the molten fatty matter. The admission of steam is continued for from twenty-four to thirty-six hours according to the kind of fat. The saponification proceeds regularly and the products distil over and are collected at the lower aperture of the cooling apparatus. The fatty acids are at once fit for candle-making purposes, while the glycerine is purified by a subsequent distillation with steam. As already mentioned, the proper temperature has to be scrupulously maintained, for if the temperature falls below 310°, the saponification proceeds very slowly; but if the temperature rises much above that degree, a portion of the fatty substance is decomposed and acroleine is formed in large quantity.

H. Heckel describes a simple apparatus for the purpose.

According to Korschelt the decomposition is much facilitated if the fat is finely divided before exposure to the steam. The fat is heated for this purpose in a receiver, *A* (Figs. 593 and 594), to 100° and passes thence into a wrought-iron pipe, *a*, with

Fig. 593.

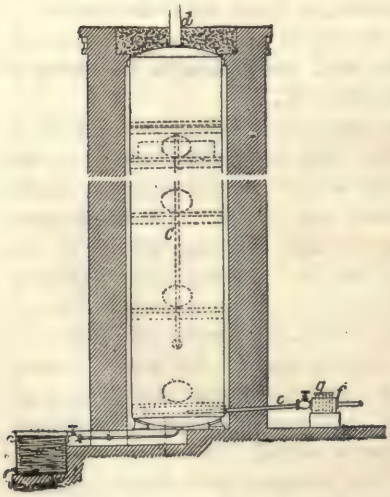
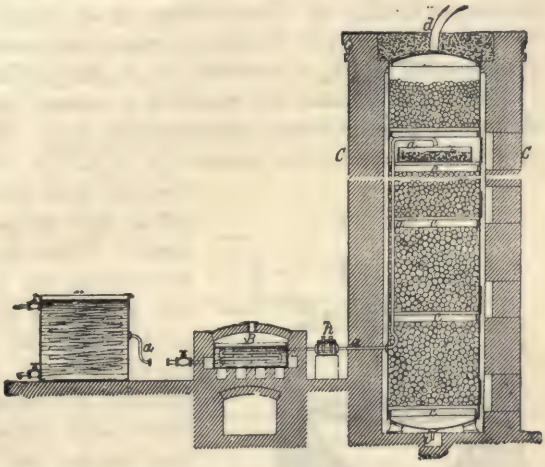


Fig. 594.



many curves which lies in the metal bath, *B*. The latter consists of a strong iron vessel in which lead and an alloy of lead and tin (preferably an alloy melting at 290°, of 100 parts lead with 6 or 7 tin) is kept in a molten state. The oil issues from this bath at about 300° and arrives in the tower, *C*, in which the decomposition is effected. The tower is built of cast-iron plates surrounded with masonry, but with an isulating stratum of air between, and is filled with balls of burnt clay, &c., lying on gratings, *e*. The hot oil is forced upwards through a pipe, *a*, which ascends in the middle of the tower and flows through the descending end of this tube upon a distributor, *n*. From this the oil pours over the clay balls and flows down among them, coming thereby in intimate contact with superheated steam introduced into the tower through the pipe, *c*, and rising upwards. The glycerides are thus split up into free fatty acids and glycerine, and these products of decomposition pass along with the steam through exit tube, *d*, to a suitable refrigerator. Into the tube, *c*, conveying the superheated steam a box, *f*, is inserted in which are fixed two or more tubes, *g*, open above and

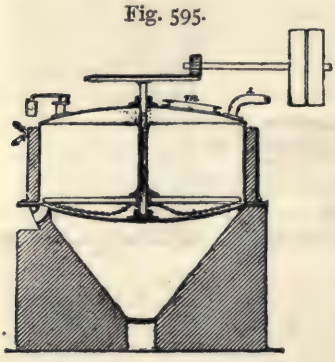
closed below; one of these is filled with lead (melting point 334°); the second with an alloy of 100 parts lead with 6 parts tin (melting point 289°) and a third with zinc (melting-point 412°), so that the observation of these tubes renders it possible to estimate the temperature of the steam entering the tower. A similar arrangement, *h*, is introduced into the oil-pipe, *a*. The inflow of the oil is so regulated that little or none arrives at the bottom of the tower undecomposed. The oil which collects there is conveyed away by the pipe, *i*, passes through the worm, *s*, into the condenser, *m*, and runs away into a receiver. If fats are used which are solid at common temperatures a little steam is allowed to enter through the tube, *i*, or the condensing water is raised to the required temperature in some other way.

For some years the process proposed by Bock has been in use for the saponification of fats. He treats the fat with sulphuric acid at a moderate temperature and without distillation. By this treatment the albuminous membranes in which the fat globules are enclosed and which make up 1·0 to 1·5 per cent. of the fat are destroyed and the fat may be decomposed by simply boiling with water in open vessels. According to Birnbaum the mixture of fatty acids thus obtained contains 99·53 per cent. fatty acid without a trace of glycerine. Hartl, of Vienna, carries out this process in an improved form.

Conversion of Oleic Acid into Palmitic Acid.—Tallow generally yields about 50 per cent. of oleic acid which scarcely fetches half the price of the solid acids. The conversion of oleic acid into solid palmitic acid which was formerly carried out by Cramer and then on the large scale by Radisson, of Marseilles, is based upon the reaction—discovered in 1841 by Varrentrapp—of an excess of caustic potassa upon oleic acid, the latter being split up into palmitic acid, acetic acid and hydrogen according to the equation, $C_{18}H_{34}O_2 + 2KOH = C_{16}H_{31}KO_2 + C_2H_3KO_2 + H_2$.

On the large scale the re-action is effected in cast-iron cylinders with covers of sheet-iron, three metres in diameter (Fig. 595). Into these are pumped about 1·5 ton of oleic acid and 2·5 ton potassa lye of 80° Tw., and heated by a fire placed at such a distance as to prevent overheating. The steam given off at first escapes through the man-hole *m* in the cover. When the soap becomes dry the man-hole is covered and the escaping gases are conveyed through the pipe *z* to the condensing tower and then to a gas-holder. The temperature of the mass is slowly raised to 290°. An agitator keeps the mixture in constant movement. At 290° the escape of hydrogen begins after the soap is melted. When the temperature reaches 320° the escaping gases have a peculiar smell. The operation must then be at once ended, as otherwise decomposition would ensue. Steam and water are therefore let into the cylinder, and at the same time a trap at the bottom is opened through which the potassium palmitate falls into water, where it is boiled by means of steam with a certain quantity of water. On settling, the product separates into two layers, the upper of neutral potassium palmitate, and the lower of potassa-lye at about 27° Tw. Potassium palmitate is decomposed by sulphuric acid in another vessel, yielding a pale-brown palmitic acid which on cooling forms large tabular crystals. After crystallisation it is perfectly white, burns with a luminous smokeless flame, and is equal to the best quality of stearic acid. If mixed with common stearic acid it loses the tendency to crystallise and has a translucency which is much esteemed in the candle trade. An attempt has been made to decompose the palmitate by boiling with milk of lime in order to recover the potassa. But it is necessary to work with a solution at 8·5° Tw., and the expense of concentration to 80° Tw. is far from insignificant.

Fig. 595.



By this process oleic acids from the most different sources may be converted into solid acids excepting that from mare's fat and from the suint of wool. Oleic acid prepared by Bock's process gave the best yield—*i.e.*, 94 to 95 per cent. palmitic acid. The cost of the conversion amounts at Marseilles to 31·15 francs for 100 kilos. of white palmitic acid.

The substition of soda for potassa in this process presented at first some difficulties, since sodium oleate is relatively difficultly fusible and is a bad conductor of heat, so that a uniform temperature of the melted salt could not be obtained even by the use of an agitator. Radisson found, however, that this defect might be removed by adding a certain quantity of paraffine to the mixture of soda-lye and oleic acid. The paraffine effects a perfect liquefaction of the mass and prevents the sodium palmitate from being heated above its decomposition point. The small quantity of paraffine volatilised in the operation is received in a condenser. The escaping hydrogen is so rich in hydrocarbon that it is a good gas for lighting. After the end of the operation the mass is treated with water as usual and separates into three layers, paraffine at the top, sodium palmitate in the middle, and soda-lye, containing some sodium acetate, at the bottom. The paraffine and the soda-lye are used for succeeding operations, whilst the sodium palmitate is decomposed by sulphuric acid. The conversion is so complete that the loss does not exceed 1 per cent.

Glycerine.—Glycerine, $C_3H_8O_3$ (a triatomic alcohol, $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$, or $C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right)$, is present in the shape of glycerides in combination with solid and fluid fatty acid to an amount of 8 to 9 per cent., and may be separated by treatment with bases (potash, soda, lime, baryta, lead oxide), or with acids (sulphuric acid), and certain chlorides (*e.g.*, zinc), also by means of superheated steam, or very hot water without the formation of steam, in closed vessels. Glycerine is also formed as a constant product by the alcoholic fermentation of dextrose, levulose, and lactose. According to Pasteur's researches, the quantity of glycerine thus formed amounts to about 3 per cent. of the weight of the sugar. Glycerine was first discovered by Scheele whilst engaged in preparing lead plaster. Industrially, glycerine has been used for only twenty-five years, in consequence of the large quantity of glycerine now obtained as a bye-product in the manufacture of soap as well as of stearine candles. The vinasse of the potato, and molasses from beet-root sugar distillation, and likewise the residue of the distillation of wine, vinasse proper, as carried on in the South of France, contain large quantities of glycerine.

As regards the preparation of glycerine on the large scale, it is mainly a question of purification of the glycerine obtained in the industrial preparation of the stearic acid from neutral fats above described. When the lime saponification process is used, the glycerine remains dissolved in the water after the separation of the insoluble lime-soap. The dissolved lime having been eliminated by either sulphuric or preferably oxalic acid, the evaporation of the liquid to the consistency of a syrup will yield a glycerine pure enough for many technical purposes. When the decomposition, or rather dissociation, of the neutral fats is effected by means of superheated steam, the glycerine and fatty acids are both obtained in a pure state, provided the heat be kept at or below 310°, because otherwise a portion of the glycerine is decomposed with evolution of vapours of acroleine. The fact that, when fats are saponified with sulphuric acid, the sulphoglyceric acid in aqueous solution yields readily by evaporation glycerine and sulphuric acid, may be applied for the preparation of glycerine. The soapboiler's mother liquor, now the most important source of crude glycerine, may be made available for its production, according to Reynold's patent, in the following manner:—The mother liquor is first concentrated by evaporation; the saline matter which is thereby gradually separated being removed from time to time. When the

fluid is sufficiently concentrated—ascertained by the boiling point having risen to 116°—it is transferred to a still, and the glycerine distilled off by means of superheated steam carried into the still. The distillate is next concentrated and brought to the consistency of a syrup in a vacuum pan.

The boiling-point of glycerine is 290°. The glycerine, freed from colouring matters, if necessary by means of animal charcoal, cannot be brought to the necessary concentration in open vessels without becoming coloured. It is therefore allowed to flow into a vacuum pan, in which it is concentrated in the absence of air. Frequently, however, a re-heating with animal charcoal and a filtration are needed. Dynamite works require a glycerine free from chlorine; for this purpose it is purified with silver nitrate.

The distillation of glycerine for its purification, as indicated by Wilson and Payne in 1855, forms a great advance in the manufacture.

The glycerine, after being entirely, or almost entirely, freed from fatty acids, is distilled with superheated steam in the absence of air, when the steam also serves to expel volatile impurities. A current of steam at from 100° to 110° is then passed for several hours, by means of a perforated tube, through glycerine, which has been previously brought at the lowest possible temperature to sp. gr. 1·15, until the products passing over have no longer an acid reaction. It is then heated (while still introducing superheated steam) to from 170° to 180°, but not above 200°. If necessary, it may be rectified in the same manner. It is important that glycerine should be separated from the accompanying water by fractionated refrigeration, to a degree sufficient for all technical purposes. By distillation with heated steam there is obtained, not an aqueous solution of glycerine, but, if the vapours are passed into a series of refrigerators surrounded with bad conductors of heat, in the first, a glycerine which is nearly anhydrous, in the following, water, containing little glycerine, and in the last, water which has scarcely a sweet taste. These liquids are used for diluting glycerine which is to be refined

Pure glycerine has the sp. gr. 1·2653; it takes fire if heated to 150°, and burns with a blue, faintly luminous flame; it burns also with a wick. The freezing of glycerine was observed by W. Crookes, of London, in 1867, by Sarg, of Vienna, and by Woehler, of Göttingen.

Among the many applications of glycerine are the following:—For keeping clay moist for modelling purposes; for preventing mustard from drying up; for keeping snuff damp; preserving fruit; sweetening liqueurs; and for the same purpose for wine, beer, and malt extracts. Glycerine is also useful as a lubricating material for some kinds of machinery, more especially watch and chronometer works, because it is not altered by contact with air, does not become thick at a low temperature, and does not attack such metals as copper, brass, &c. Glycerine is used in the making of copying inks, and of a great many cosmetics. In order to render printing ink soluble in water—its insolubility is, however, its greatest advantage—it has been proposed to use glycerine for its preparation instead of linseed oil. Glycerine is an excellent solvent for many substances, including the tar-colours (aniline blue, cyanine, aniline violet) and alizarine.* In order to render paper soft and pliable glycerine is added to the pulp. To the quantity of pulp required for making 100 kilos. of dry paper, 5 kilos. of glycerine, sp. gr. 1·18, are sufficient. It is not out of place here to mention the following useful weavers' glue or dressing, composed of—Dextrine, 5 parts; glycerine, 12 parts; ammonium sulphate, 1 part; and water, 30 parts. By the use of this mixture the weaving of muslins need not be—as was formerly the case—carried on in damp, darkened cellars, but may be performed in well-aired and well-lighted rooms. It is said that leather driving-belts, made as usual of weakly tanned leather, when kept in

* In dyeing with colouring matters of great tinctorial power, such as many coal-tar colours, glycerine is an excellent addition to the dye-beck. It prevents "flurry," *i.e.*, the formation of a coloured froth or scum on the surface, which is a frequent cause of unevenness.—[EDITOR.]

glycerine for twenty-four hours, are not so liable to fray. A glycerine solution is now largely used instead of water for the purpose of filling gas-meters, as such a solution does not freeze in winter nor evaporate in summer. Santi uses glycerine for the compasses on board screw-steamers, in order to protect the inner compass-box against the vibrations caused by the motion of the propeller. It is impossible to enter here into minute details on the use of glycerine. Suffice it to observe further, that it is employed for preserving anatomical preparations, for rendering wooden casks impervious to petroleum and other oils; for the preparation of artificial oil of mustard or sulpho-cyan-allyl, made by treating glycerine with phosphorus iodide, whereby allyl iodide is formed, which on being dissolved in alcohol, and next distilled with potassium sulphocyanide, yields sulpho-cyan-allyl. When glycerine is treated with very concentrated nitric acid or with a mixture of strong sulphuric and nitric acids, it is converted into nitro-glycerine (trinitrine or glyceral nitrate) (see p. 393), largely used for various purposes, the preparation of dualine and dynamite, &c. A mixture of finely powdered litharge and very concentrated glycerine, made into a paste, forms a rapidly hardening cement, especially useful as a cover for the corks or bungs of vessels containing such fluids as benzol, essential oils, benzoline, petroleum, &c., the cement being impermeable to these liquids.

When used for sweetening wines or liqueurs, it is sold under the incorrect name of saccharine, and its application is known as "scheelising."

ESSENTIAL OILS AND RESINS.

These substances almost all occur naturally. To the essential oils most plants owe their odour and flowers their perfume. The essential oil in plants is met with enclosed in cells; hence, after bruising a plant, or the parts containing the essential oil, the peculiar odour is more perceptible; for instance, by gently rubbing between the fingers the leaves of some kinds of geraniums, melissa, lemon plant, &c. Essential oils do not impart to the fingers a fatty, but a rather rough, harsh feeling. A large number of essential oils possess the property of precipitating silver from its ammoniacal solution in a metallic state; hence the use of essential oils in silvering glass (see p. 614).

Preparation of Essential Oils.—These oils are chiefly obtained by submitting parts of plants, previously ground to a coarse powder, to distillation with water. Although the boiling point of these oils is generally much higher than that of water, the oils are mechanically carried over in a minute state of division with the aqueous vapour. When oils, the boiling point of which is very high, have to be extracted, some common salt is added to the water to heighten its boiling-point. In order to separate the oil from the water, there is employed a peculiarly shaped vessel, called a Florentine flask. In this way the essential oils of aniseed, chamomile, lavender, peppermint, cloves, cinnamon, &c., are obtained, while the most common essential oil—viz., that of turpentine—is obtained by the distillation of Venice turpentine with water.

Preparation of Essential Oils by Pressure.—The essential oils largely met with enclosed in the cells of the skin of lemons, oranges, bergamots, and, in fact, all the fruits belonging to the *Citrus* genus, are obtained by pressing the rinds of these fruits. Although the greater number of the essential oils occur ready formed in various parts of the plants, some of these oils are the result of the action of water—as, for instance, the essential oil of bitter almonds, which is formed by the action of water upon amygdalin under the influence of a peculiar albuminous compound called synaptase or emulsin; the essential oil of mustard seed is formed in a similar manner, but may be artificially prepared by distilling a mixture of propyl iodide and potassium cyanide, &c.

Extraction of Essential Oils by Means of Fatty Oils.—Some of the essential oils, more especially those present in flowers, are so sparingly distributed, that they can only be obtained by digesting the fresh flowers with pure olive oil or with cotton-wool soaked in sweet olive oil, the fresh flowers being placed in alternate layers between the cotton saturated with oil; in some cases pure lard is employed. The essential oils may be recovered from the sweet oils by agitation with strong and highly rectified alcohol. The essential oils of jasmine, sweet violets, hyacinths, &c., are obtained in this manner.

Properties and Uses of Essential Oils.—These oils are more or less soluble in water, and the solutions are known in pharmacy as distilled waters. The essential oils are soluble in alcohol in proportion to the amount of oxygen they contain. Upon this property is based the use of these oils in perfumery and for the preparation of liqueurs (cordials).

Perfumery.—This branch of industry provides us with scented waters (*esprits eaux de senteur*), odoriferous extracts (*extraits à odeurs*), perfumed fats, pomatums, oils, &c. Scented waters are really alcoholic solutions of one or more essential oils. The alcohol used for this purpose requires to be very pure and perfectly free from fusel oil or other impurity. The oils are dissolved in the alcohol, and in order to blend the mixture and render it mellow, it is kept for several months in a bottle before being sold. The old process of distillation is very properly discarded, because, owing to the high boiling point of the oils, a portion was left in the still, while the scented waters thus prepared were inferior in quality. *Eau de Mille Fleurs* is prepared by dissolving in 9 litres of alcohol, 60 grammes of balsam of Peru, 120 grammes of oil of bergamot, 60 grammes of oil of cloves, 15 grammes of neroli oil (oil of orange-flowers, a very expensive oil), 15 grammes of oil of thyme, adding to the mixture 4 litres of orange-blossom water, and 120 grammes of tincture of musk, obtained by digesting 15 to 25 grammes of civet and 75 grammes of musk with 2 litres of alcohol. *Eau de Cologne* is obtained by dissolving in 6 litres of alcohol 32 grammes of essential oil of orange-peel and equal quantities of oil of bergamot, lemon, *essence de limette*, *essence de petit grains*, 16 grammes *essence de cedro*, and equal quantities of *essence de cedrat* and *essence de Portugal;* further, 8 grammes of neroli oil and 4 grammes of rosemary. The perfumed extracts are generally obtained by the exhaustion, by means of alcohol, of the scented fats and oils prepared from flowers as before described.

Artificial Perfumes.—Doebereiner first suggested the use of artificial perfumes; among these are an alcoholic solution of amyl acetate as pear oil, amyl valerate as apple oil, amyl butyrate as pineapple oil, ethyl pelargonate as quince oil, ethyl suberate as essence of mulberries, while nitrobenzol mixed with nitrotoluol (commercial nitrobenzol) is termed artificial oil of almonds, and, when very coarse, is sold as *essence de mirbane*, chiefly used for the preparation of aniline. The perfumed fats (pomatums) of better quality are generally prepared from an infusion of the flowers with oil or fat at a temperature of 65°, or by a process of digestion in the cold by placing the flowers in layers between pure lard or cotton-wool soaked in very pure olive oil; *enfleurage* is the name given to this operation. The ordinary pomatums are made simply of lard or marrow-fat coloured with turmeric, annatto, or alkanet root, and perfumed with a few drops of some essential oil.*

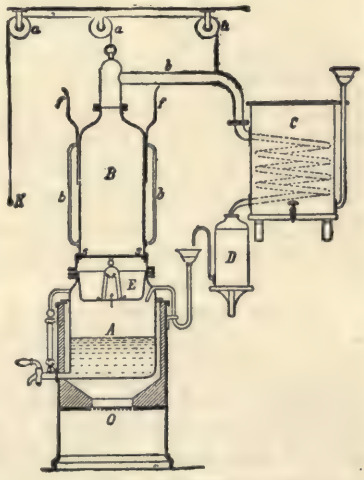
Preparation of Cordials.—The aim of the preparation of liqueurs (cordials) is to render brandy a more agreeable beverage by the addition of sugar, glycerine, and aromatic substances. A distinction is made between the finer liqueurs [*rosoglio*) and

* The reader may here consult Piesse's "Art of Perfumery." 5th edit. London: Piesse & Lubin. It is not demonstrated that the artificial perfumes made according to Doebereiner's process agree in their physiological action with the natural products which they simulate.—[EDITOR.]

ordinary cordials (*aqua vitæ*) according to the quality of the materials employed for the purpose. When a sufficiently large quantity of sugar is used to render the liqueurs thickly fluid they are designated *crêmes*, while those made with the juices of fruit obtained by pressure, sugar and alcohol are called ratafia. These liqueurs are not prepared to any great extent in this country; but in France, Italy, Austria, and especially in Holland, the preparation is on a large scale.

The basis of all liqueurs is a very highly rectified and pure alcohol. The vegetable materials used in the liqueurs may be classified under three heads:—In the first place, such vegetable substances as contain essential oils and are used for that reason only, caraway, aniseed, juniper-berries, mint, lemon-peel, orange-blossom, and bitter almonds. These substances, previously bruised or cut up, are digested with alcohol, the mixture being next distilled, or, as is more generally the case, alcoholic solutions of the essential oils are employed and the preparation performed in the cold. To the second class belong such vegetable substances as are used for the sake of their essential oil and for their aromatic bitter substances, chiefly roots, such as sweet calamus, gentian, ginger, orange-peel, unripe bitter Curaçoa apples (a peculiar kind of orange), wormwood, cloves, cinnamon, vanilla (the pod of an orchidaceous plant originally brought from Mexico). These substances having been bruised are digested with alcohol either at the ordinary temperature of the air or at 50° or 60°, the result being the formation of what is termed a tincture. To the third class belong fruits, such as cherries, pineapples, strawberries, raspberries, the juice of which is obtained by pressure, passed through a sieve, and mixed with alcohol and sugar or syrup, viz., a solution of 4 lbs. of refined loaf-sugar in 4 litres of water. The liqueurs generally contain from 46 to 50 per cent. of alcohol. It is customary to colour the liqueurs red with santal-wood, cochineal, aniline red, or with the *Coccus polonicus*, as in the case with the celebrated Alkermes de Firense, a liqueur made at Florence; yellow with saffron, turmeric, or marigold flowers (*Calendula*); green by mixing yellow and blue; blue, with tincture of indigo; violet, with aniline violet; while in many cases caramel is used to impart a brown colour. The so-called *crêmes* contain for every litre of liquid about 1 lb. of sugar or a corresponding quantity of glycerine. As an instance of the composition of a liqueur, Maraschino consists of 4 litres of raspberry water, 1·75 litres orange-blossom water, 1·5 litres kirschwasser (a Swiss preparation — from cherries fermented and distilled—a strong, spirituous liquid which contains hydrocyanic acid), 18 lbs. of sugar, and 9 litres of alcohol at from 89 to 90 per cent. Liqueurs are very similar to *crêmes*, but contain less sugar. English bitter contains 5 parts of *flavedo corticum aurantiorum* (outer rind of dried orange peel), 6 parts of cinchona bark, 6 parts of gentian, 8 parts of *Carduus benedictus*, 8 parts of centaury, 8 parts of wormwood, 4 of orris root digested with 54 litres of alcohol at 50 per cent., while after filtration 12 lbs. of sugar are added. Cherry ratafia:—20 litres of cherry juice, 20 litres of alcohol at 85 per cent., 30 lbs. sugar, and usually 4 to 8 litres of bitter almond water. Peppermint:—2·5 litres of essential oil of peppermint dissolved in 1 litre of alcohol at 80 per cent.; this solution is poured into 54 litres of alcohol at 20 per cent., sweetened with 60 lbs. of sugar previously dissolved in 26 litres of water, and coloured with either tincture of indigo or turmeric.

Fig. 596.



In Mürrle's apparatus for the extraction of ethereal oils (Fig. 596) there is suspended a copper boiler, *A*, in the round iron furnace, *O*. Steam enters through the tube, *E*, into the receiver, *B*, on the perforated bottom of which, *s*, the plants are laid, and it escapes then with the ethereal oil through the pipe, *b*, into the worm, *C*. The distillate collects first in the Florentine receiver, *D*, where the ethereal oil separates out at the top whilst the water, being heavier, flows back through the bent tube-funnel into the boiler, *A*, to be evaporated anew. The distillation is continued until the water escaping from the worm is scentless. When the distillation is at an end the capital is detached and raised by means of the tackle, *K*, when the receiver, *B*, can be lifted off the two handles, *b*, *b*. The perforated bottom is taken out downwards and the residue is then thrown away. The charging can also be executed rapidly, the upper aperture being closed by the accompanying screw lid and *B* being inserted, in which position it stands on its three feet, *f*. When *B* is filled the perforated bottom is introduced, the whole is inverted and replaced upon the boiler, *A*. By providing a second receiver, *B*, of the same size, the working power of the apparatus can be increased, as one receiver is at work whilst the other is being emptied and filled again. The catch-pan, *E*, prevents any extractive matter from falling down into the boiler, *A*, burning and spoiling the odour of the essential oil.

In the process of *enfleurage* it has lately been proposed to use chlormethyl instead of fatty oils.

The artificial essences simulating the odour of certain natural perfumes may be legitimately used in cosmetics, &c., but it is at least doubtful whether their physiological action is identical with that of the natural products which they imitate. Hence their use in the production of liqueurs is questionable.

Resins.—By the action of the oxygen of the air most of the essential oils are gradually thickened, and at length converted into a substance termed resin. Resins are frequently met with in the vegetable kingdom; in some instances, as with coniferous trees, resin flows spontaneously from the wood in combination with an essential oil, so-called Venice turpentine, which hardens by exposure to air. Some resins are extracted from vegetable matter by means of alcohol, this solution being either precipitated with water or evaporated to dryness. Resins are either soft, and are then termed balsams, chiefly solutions of resin in essential oils, or hard. To the former belong Venice turpentine, Canada balsam, balsam of Peru, copaiva balsam, &c.; to the latter, amber (a fossil resin), anime, copal, gum dammar, mastic, shellac, asphalte. The gum resins are obtained from incisions made in certain kinds of plants, the milky juice of which hardens by exposure to air; these substances are partly soluble in water, and yield with it in many instances an emulsion; for instance, asafœtida, gum gutti, &c. Many gum resins possess a very strong odour and contain essential oils. Although it is customary to treat of caoutchouc and gutta-percha under the head of resins, these substances are not related to resins at all, but belong to a separate class of bodies, among which, according to Dr. G. J. Mulder's researches, the so-called drying oils must be enumerated.

Sealing-Wax.—Sealing-wax of modern time (for mediæval sealing-wax was really a mixture of wax with Venice turpentine and colouring matter) is prepared from shellac, to which some turpentine is added in order to promote fusibility and prevent brittleness. Red sealing-wax and bright coloured wax are made of a very pale, sometimes even purposely bleached, shellac, while black and dark coloured sealing-wax are made of more deeply coloured shellac. In addition to shellac and turpentine, sealing-wax contains earthy matter, added not only for the purpose of increasing the weight, but also for preventing the too rapid fusion of the mass; chalk, magnesia, plaster of Paris, zinc-white, barium sulphate, kaolin, and finely divided silica, are employed for this purpose. Red sealing-wax is prepared by melting together in an iron pan placed on a

charcoal fire 4 parts of shellac, 1 part of Venice turpentine, and 3 parts of cinnabar (vermilion), care being taken to stir the mixture constantly. Ordinary red sealing-wax is often composed of:—

	1.	2.	3.	4.	5.
Shellac	550	620	550	700	600
Venice turpentine	740	680	600	540	600
Chalk or magnesia	300	200	—	—	—
Gypsum or zinc-white	200	—	—	—	—
Baryta white	—	100	380	300	300
Vermilion	130	220	340	300	300
Oil of turpentine	—	—	—	20	25

The cooled but still soft mass is either rolled on a slab of marble and shaped into sticks, or the fluid mass is run into brass moulds. Perfumed sealing-wax contains either benzoin resin, storax, or balsam of Peru. The various colours are imparted by cobalt ultramarine (cobalt blue), lead chromate, bone-black, &c. Marbled sealing-wax is made by mixing variously coloured sealing-waxes together. Inferior kinds of sealing-wax—parcel-wax—are coloured with red oxide of iron, while instead of shellac ordinary resin is used with gypsum or chalk. New Zealand resin, the produce of the *Xanthorrhœa hastilis*, is now frequently used instead of shellac.

Asphalte.—This material, sometimes known as bitumen, is a black, glossy, brittle resin, probably formed by the gradual oxidation of petroleum oil; it occurs very largely on the island of Trinidad, on the northern coast of S. America, at the mouth of the Orinoco, on the water of the Dead Sea (anciently *Lacus Asphaltites*), and in some other localities—viz., France, Seyssel, Department de l'Ain, a limestone containing 18 per cent. of asphalte. By boiling this limestone, previously broken up into small lumps, with water, there is obtained an asphalte, 7 parts of which are mixed with 90 parts of native asphalte limestone. The materials are ground up together and are employed for paving purposes, being compressed with heavy and highly heated irons. Asphalte is also found at Val de Travers, Switzerland; Limmer, Hanover; Lobsann, Lower Alsace; and in the Northern Tyrol. Asphalte, or bitumen, is somewhat soluble in alcohol, readily so in Persian naphtha, oil of turpentine, benzene, and benzoline. It is used in varnish making (iron varnish), in engraving copper and steel, as an etching ground, and as an oil paint. Asphalte mixed with sand, lime, or limestone, is largely used for paving purposes, being durable and somewhat elastic; it is employed for this purpose either in a pasty or semi-fused state, or in powder. Instead of native asphalte, Busse's terresin, a mixture of coal-tar, lime, and sulphur is sometimes used, as well as coal-tar asphalte, obtained from gas works. The residue of the distillation of coal-tar is often employed instead of asphalte, and pebbles mingled with coal-tar are now used to form excellent footpaths in some parts of the metropolis.

Tubes of paper, saturated with asphalte, are often used for water-, gas-, and drain-pipes. Sheets of strong paper and pieces of woven cloths steeped in asphalte are used for roofing.

Caoutchouc.—Elastic gum, or india-rubber, is derived from the milky juice of a series of plants, occurring also in opium; but the commercial article is obtained from the milky juice of various trees belonging to the natural orders of the *Urticeæ*, *Euphorbiaceæ*, *Apocyneæ*. Among the trees which yield caoutchouc in large quantity are the *Siphonia cahucu*, in South America, and the East Indian species, *Urceola elastica*; *Ficus elastica*, *F. religiosa*, *F. indica*, also yield caoutchouc. It is obtained by making incisions in the tree and collecting the exuding juice in vessels of dried clay. The juice is solidified by the application of fire or by exposure to the sun's rays; the variety known as lard gum is usually dried by exposure to the sun. Perfectly pure caoutchouc is a white, and in thin sheets semi-transparent, substance; its texture is not fibrous;

it is perfectly elastic, becoming turbid and fibrous when strongly stretched. Excessive cold renders it hard but not brittle. The specific gravity of caoutchouc is 0·925. Although hot water and steam render caoutchouc soft, it is not further acted upon by them. It is insoluble in alcohol, not acted upon by dilute acids or strong alkalies, while for a very long time it resists the action of chlorine. Strong sulphuric and nitric acids decompose india-rubber, and when red fuming nitric acid is employed a violent combustion ensues. If strongly stretched india-rubber is placed in cold water for a few minutes it temporarily loses its elasticity, which it regains by being immersed for a few minutes in water at 45°. By exposure to a gentle heat caoutchouc becomes supple, and finally melts at 200°, with partial decomposition, forming a viscous mass which does not again become solid on cooling. When caoutchouc is ignited in contact with air it burns with a sooty flame. Of all substances with which we are acquainted none would be better suited to gas manufacture than caoutchouc, which, according to experiments made many years ago at Utrecht, yields at red heat rather more than 30,000 cubic feet of gas to the ton, the gas being quite free from sulphur and ammonia compounds, and its illuminating power very superior to that of the best oil gas. Unfortunately caoutchouc is much too high priced for this application. Caoutchouc may be kneaded with sulphur and other substances by the aid of heat, becoming converted into what is known as vulcanised india-rubber, vulcanite, ebonite, &c. When caoutchouc is submitted to dry distillation, at much below red heat, it yields only oily fluids, consisting of carbon and hydrogen (caoutchen, heveen, &c.), which are *par excellence* solvents for caoutchouc. Caoutchouc itself contains only carbon and hydrogen, its formula being C_4H_7 (in 100 parts: 87·5 carbon and 12·5 hydrogen); probably, however, caoutchouc is a more complex mixture of various hydrocarbons.

Solvents of Caoutchouc.—India-rubber is soluble in ether containing no alcohol, in the oils (empyreumatic) of caoutchouc, in Persian naphtha, oil of turpentine, carbon disulphide, and in chloroform. Industrially the ethereal solution of caoutchouc is useless, because it contains hardly more than a trace of that substance. As regards oil of turpentine, it dissolves caoutchouc only when the oil is very pure and with the application of heat; the ordinary oil of turpentine of commerce causes india-rubber to swell rather than to become dissolved. In order to prevent the viscosity of the india-rubber when evaporated from this solution, 1 part of caoutchouc is worked up with 11 parts of turpentine into a thin paste, to which is added ½ part of a hot and concentrated solution of potassium sulphide (K_2S_5) in water; the yellow liquid formed leaves the caoutchouc perfectly elastic and without any viscosity. The solutions of caoutchouc in coal-tar naphtha and benzoline are most suited to unite pieces of caoutchouc, but the odour of the solvents is perceptible for a long time. As chloroform is too expensive for common use, carbon disulphide is the most usual and also the best solvent for caoutchouc. This solution, owing to the volatility of the menstruum, soon dries, leaving the caoutchouc in its natural state. When alcohol is mixed with carbon disulphide, the latter no longer dissolves the caoutchouc, but simply softens it and renders it capable of being more readily vulcanised. Alcohol precipitates solutions of caoutchouc and gutta-percha.

The great diversity of the sorts of caoutchouc, according to Hoehnel, is not merely external, but extends to their essential properties, and is due both to the different methods of preparation and to the fact that the commercial article is derived from upwards of fifty plants, belonging to different families.

The methods of preparing caoutchouc from the milky juice are as follows:—(1) The juice is poured upon a mould in thin layers, and these layers are gradually dried in hot smoke. More than one hundred layers are thus often produced. (2) The milky juice is conveyed directly from the tree to small pits made in the soil. The soil acts as a filter;

the watery part of the milk filters off or partly evaporates, whilst the caoutchouc remains behind. This method is very crude, and can be applied only in the dry season. (3) The milky juice is mixed with a little water and allowed to stand for some days to coagulate. The mass thus separated out is freed from excess of water by kneading and pressing, and then dried in the sun or in smoke. (4) The milky juice is mixed with a solution of salt or of alum, with an acid, or with the extract of certain plants, whereon it quickly curdles; the clot is then pressed and dried. (5) The milky juice is mixed with 4 to 8 parts of water, when the caoutchouc comes to the surface like a thick cream, which is collected, repeatedly washed, and dried either in smoke or very slowly in the air. (6) The milky juice is simply allowed to dry in shallow vessels. (7) The milky juice is concentrated, and is caused to flow down upon the arm of the collector, where it quickly dries, and is rolled off in the form of a ring. (8) Or the concentrated juice flows down upon the stem or drops to the ground, where it is collected and moulded into balls.

The most valuable kinds known in commerce, the "Para," are obtained by the first process. The same method is in use in Columbia. Para caoutchouc consists of strata generally less than $\frac{1}{2}$ mm. in thickness, white or dark grey, and it appears separated by sharp black lines where it has been exposed to smoke; the finer and the more equal these layers are—which may be seen on section—the better is the sample. Inclosed air-bubbles signify an inferior quality. As soon as there are seen layers from 1 to 2 centimetres in thickness, white, and full of bubbles, we have a second-rate Para. The second process is in use in Columbia, Central America, and occasionally, along with other methods, in Africa and Southern Asia; it yields a watery, contaminated, inferior product. The processes (3) and (4) yield an article rich in water, often containing uncoagulated milky juice. Those kinds are especially bad which have been coagulated by the addition of foreign matter, salts, &c. Coagulation is practised in the north of South America, in Central America, West Africa, India, and the Sunda Islands. These kinds are often dried too rapidly, and have therefore a black surface, smelling of smoke and sometimes are even burnt. If the drying is too rapid, the surface remains smeary. Such sorts are named resinous, and are often found in Indian, West African, and Central American lots. It must not be forgotten that South Asiatic samples are often artificially contaminated with resins or vegetable extracts. Such resinous sorts are in very low estimation. Recent samples of qualities obtained by coagulation show on section a homogeneous grey rind, a few millimetres in thickness, and a thick, white, violet, yellow, or flesh-coloured nucleus, which is quite soft and often contains water or milky juice. The sorts obtained by coagulation are poor in fragments of wood and bark, which occur most abundantly in sorts prepared by methods (7) or (8). Process (5) is used in some parts of Central America, and yields a good quality. Process (6) gives a similar product, highly esteemed, and imported from the Gaboon and from India.

Preparation and Use of India-rubber.—India-rubber is used to clean paper, to rub out black-lead pencil marks, for making waterproof fabrics (macintosh), rubber sponge, tubing, elastic webs, lutes, &c.*

Vulcanised Caoutchouc.—When caoutchouc is immersed for some time in molten sulphur it absorbs the latter, and becomes converted into a yellow, very elastic mass. The most valuable property of vulcanised india-rubber is its elasticity even at low temperatures; ordinary india-rubber hardens at 3°. Vulcanised india-rubber is insoluble in the solvents of caoutchouc. It resists compression to a very great extent; hence its use instead of steel springs on tramcars. According to the old method, caoutchouc

* The most important of all the uses of caoutchouc at present is in the insulation of electric wires and cables. It is the preferable ingredient in all cases when the conduction traverses a dry medium, such as air, dry earth, the interior of houses, &c.—[EDITOR.]

was vulcanised by being placed for some ten to fifteen minutes in thin plates in molten sulphur heated to 120°, the weight of the caoutchouc increasing 10 to 15 per cent. The material was subsequently mechanically treated by pressure, and then heated to 150°. In order to prevent efflorescence of the sulphur, caoutchouc is sometimes heated to 120°, and then kneaded by the aid of powerful machinery, with either kermes (Sb_2S) or a mixture of sulphur and arsenic sulphide. At the present day Parkes's method is generally adopted: the caoutchouc is simply immersed in a mixture of 40 parts of carbon disulphide and 1 part of sulphur chloride; it is next placed in a room heated to 21°, and when all the carbon disulphide has been volatilised, the process is in so far complete that it is only requisite to boil the material in a solution of 500 grammes of caustic potassa to 10 litres of water, the vulcanised caoutchouc being next washed to remove excess of alkali. In 1870 Humphrey introduced the use of petroleum ether (benzoline) instead of carbon disulphide, as the former fluid dissolves sulphur chloride readily. H. Gaultier de Claubry (1860) vulcanised caoutchouc by the aid of bleaching-powder and flowers of sulphur. This mixture produces sulphur chloride, and the caoutchouc treated by it contains some calcium chloride. Neither this process nor that of Gérard—the use of a solution of potassium pentasulphide of 40° to 49° Tw., aided by a temperature of 150°, and a pressure of 5 atmos. or 75 lbs. to the square inch—are practically available on the large scale. Articles of vulcanised india-rubber are made of ordinary caoutchouc and then vulcanised. The uses of vulcanised india-rubber are so many and so generally known that it is hardly necessary to enumerate them.

In 1852 Goodyear discovered a process by which caoutchouc is rendered hard and wood-like, being then termed vulcanite or ebonite. This substance exhibits a black or brown colour, and is largely used for making combs, imitation jet ornaments, stethescopes, and a variety of articles. The preparation of ebonite differs from that of vulcanite only in the introduction of a larger amount of sulphur (30 to 60 per cent.), at a higher temperature, with the addition of other substances—shellac, gutta-percha, asphalte, chalk, barium sulphate, pipe-clay, zinc, antimony, or copper sulphides, &c. Ebonite is capable of taking a high polish; it does not, as is the case with horn, become rough when cleaned with hot water; and it is to some extent elastic.

For articles which require elasticity, such as artificial whalebone, walking-sticks, &c., less sulphur is used than for those which require rigidity, such as rulers, discs for frictional electric machines, &c. The hardness required cannot be obtained with less than 20 per cent., but quantities above 35 per cent. are useless, on account of the increasing brittleness. After the caoutchouc, sulphur, and the other ingredients have been duly mixed together, and the articles are moulded into the required shapes the actual combination is effected by means of steam. The articles, placed on small trucks, are run upon rails into a strong cylindrical boiler, which is then tightly closed Steam is then admitted at a pressure not exceeding $4\frac{1}{2}$ atmos. The introduction of the steam must be regulated in such a manner that the internal temperature gradually rises to 135°. From this moment a very uniform temperature must be maintained. A few degrees too high would burn the contents of the boiler; and a few degrees too low, or a fluctuation in the temperature, would render the whole work nugatory. Vulcanite mixed with sand, emery, &c., sometimes serves for the production of artificial grindstones—whetstones for sharpening scythes, sickles, and other agricultural implements. Vulcanite expands very considerably in heat, about three times as much as zinc.

The yield of caoutchouc in 1882 was 20,000 tons.

Gutta-percha.—Plastic gum, gutta- or getah-percha, gettannia gum, taban gum, is a substance in many respects similar to caoutchouc; it is the inspissated juice of the *Isonandra gutta*, a tree growing in Malacca, Borneo, Singapore, Java, Madura, and adjacent countries.

Gutta-percha was at first obtained by felling the trees and collecting the exuding juice, either in suitable vessels or in shallow pits dug in the soil, or in baskets made from banyan leaves, the juice being left to coagulate under the action of the sun. More recently the practice has been to make deep incisions in the trees, and to collect the exuding juice. The lumps of solid gutta-percha thus obtained are united by softening in hot water and by pressure. The raw gutta-percha of commerce is a dry, red, or marbled mass, not unlike leather cuttings which have been pressed together; the raw material contains as impurities some sand, small pieces of wood and bark, and sometimes other inspissated vegetable juices of less value than gutta-percha. The name gutta-percha means, in fact, Sumatra gum, this island being known in Malay language as Pulo-percha. When perfectly pure, gutta-percha is quite white, its ordinary brown colour being due to an acid insoluble in water, which is present, partly free, partly as insoluble salts (of magnesia, ammonia, potash, and manganese protoxide), of apocrenic acid; but in addition there is a small quantity of organic colouring matter. Gutta-percha is a mixture of several oxygen-containing resins, which appear to be the products of the oxidation of a hydrocarbon, the formula of which is $C_{20}H_{60}$. Payen found in gutta-percha the following substances:—75 to 80 per cent. of pure gutta-percha, 14 to 21 per cent. of a white crystalline resin termed alban, and from 4 to 6 per cent. of an amorphous yellow resin named fluavil. Previously to being used, gutta-percha is cleansed from dirt by a mechanical process of kneading in warm water, being then usually rolled into thick plates or sheets. The purified material exhibits a chocolate-brown colour, and is not transparent unless first reduced to sheets as thin as paper, when the gutta-percha is equal to horn in transparency. At the ordinary temperature of the air gutta-percha is very tough, stiff, not very elastic nor ductile. Every square inch of a strap of gutta-percha, if of good quality and as homogeneous as possible, can sustain a strain of 1872 kilos. without breaking. Its sp. gr. = 0·979. At 50° it becomes soft, and at 70° to 80° it is so soft as to be very readily moulded, while two pieces pressed together at this temperature become perfectly joined. By the aid of heat, gutta-percha can be rolled into sheets, drawn into thread, and kneaded into a homogeneous mass with caoutchouc.

Solvents of Gutta-percha.—Gutta-percha is insoluble in water, alcohol, dilute acids, and alkalies; it is soluble in warm oil of turpentine, carbon disulphide, chloroform, coal-tar oil, caoutchouc oil, and in the somewhat similar oil obtained by the dry distillation of gutta-percha. Ether and some of the essential oils render gutta-percha pasty. As already stated, this substance becomes soft in hot water, absorbing a small quantity, which is only very slowly driven off. Dry gutta-percha is a very good insulating material for electricity.

Uses of Gutta-percha.—The natural properties of this substance indicate its use as a substitute for leather, papier-maché, cardboard, wood, millboard, paper, metal, &c., in all cases not exposed to the action of heat, and where a substance is desired resisting water, alcohol, dilute acids, and alkalies. The raw material, previously to being moulded into shape, is purified, and kneaded by means of powerful machinery and with the assistance of hot water (some soda or bleaching-powder solution being added), the aim being the removal of such impurities as are only mechanically mixed with the gutta-percha, as well as the removal of some of the colouring matter, while a more homogeneous mass is produced. The purified substance is next submitted to the action of kneading machinery similar to that in use for working up caoutchouc, while it is rolled out into plates of some 3 centimetres in thickness. Gutta-percha is moulded into tubes by the aid of machinery such as are employed for making lead and block-tin tubing. Many objects are made from gutta-percha by pressing it while soft into wooden or metal moulds. By the use of a solution of gutta-percha in benzol, it may be glued to leather and similar substances. It is almost impossible to enumerate the various uses of gutta-percha. It is employed for straps for machinery instead of leather, tubes for

conveying water, pumps, pails, surgical instruments, ornamental objects of various kinds, for covering telegraph wires, &c.* Unlike pure caoutchouc, gutta-percha becomes gradually deteriorated by exposure to the atmosphere, so that ultimately it can be even readily ground to powder.†

Mixture of Gutta-percha and Caoutchouc.—Frequently a mixture of 1 part of gutta-percha and 2 parts of caoutchouc is employed. Articles made of this compound possess the properties of both substances, and may be vulcanised equally as well as gutta-percha alone. A mixture of equal parts of caoutchouc, gutta-percha, and sulphur, heated for several hours to 120°, obtains properties similar to those of bone and horn. Sometimes gypsum, resin, and lead compounds are added to this mixture, which is then used for making knife-hafts, buttons, &c.‡

Balata.—Since 1857 a product has become known which is intermediate in its properties between caoutchouc and gutta-percha, and finds similar industrial applications. Balata is obtained from the inspissated milky juice of the so-called bully-tree (*Sapota Muelleri*), a sapotaceous tree growing throughout Guiana. It is chiefly used for driving-bands, for soles and heels, and in dentistry.

Celluloid.—This name is applied to a mixture of nitro-cellulose and camphor. It has the advantage over vulcanite that it can be obtained in various colours, but it has the defect of being exceedingly combustible.

PRESERVATION OF WOOD.

On the Durability of Wood in General.—The durability of wood—*i.e.*, its power of resisting the destructive influences of wind and weather—varies greatly, and depends as much upon the particular kind of wood and the influences to which it is exposed as upon the origin of the wood (timber), its age at the time of felling, and other conditions. Beech wood and oak placed permanently under water may last for centuries. Alder wood is very lasting and substantial under water, as also is fir, though in a dry situation alder quickly perishes. Taking into consideration the different kinds and varying properties of wood and the different uses to which it is applied, we have to consider, as regards its durability, the following particulars:—

1. Whether it is more liable to decay by exposure to open air or when placed in damp situations.
2. Whether, when left dry, it is more or less attacked by the ravages of insects which, while in the state of larvæ, live and thrive in and on wood.

Pure woody fibre by itself is only very slightly affected by the destructive influences of wind and weather. When we observe that wood decays, that decay arises from the presence of substances in the wood which are foreign to the woody fibre but are present in the juices of the wood while growing, and consist chiefly of albuminous matter, which, when beginning to decay, also causes the destruction of the other constituents of the wood. But these changes occur in various kinds of wood only after a shorter or

* The last-mentioned purpose is now by far the most important. Like caoutchouc, gutta-percha is a very bad conductor of electricity, and is therefore invaluable for insulating wires which are conveying electric currents, especially if they have to be laid under water. If constantly wet it lasts a long time, but if alternately wet and dry it is inferior to caoutchouc.—[EDITOR.]

† The supply of gutta-percha has been imperilled by incautiously felling the trees. Without diligent planting and strict preservation, the *Isonandra gutta* will soon be extirpated.—[EDITOR.]

‡ It was at first expected that gutta-percha, on account of its lightness, its freedom from brittleness, and its resistance to acids, would be of great use in chemical, dye, and print works, &c., for funnels, jugs, measures, &c. It was soon, however, found that such vessels, though apparently not attacked save by concentrated sulphuric acid, became gradually disintegrated on continual use, and crumbled away. This process is much retarded, though not prevented, if the vessels are always plunged into cold water immediately after being used.—[EDITOR.]

longer lapse of time. Indeed, wood may in some instances last for several centuries and remain thoroughly sound; thus, the roof of Westminster Hall was built about A.D. 1090. Since resinous woods resist the action of damp and moisture for a long time, they generally last a considerable time; next in respect of durability follow such kinds of wood as are very hard and compact, and contain at the same time some substance which—like tannic acid—to some extent counteracts decay. The behaviour of the several woods under water differs greatly. Some woods are after a time converted into a pulpy mass. Others—*e.g.*, teak—contain caoutchouc, and are very permanent.

Insects chiefly attack dry wood only. Splint wood is more liable to such attack than hard wood; while splint of oak wood is rather readily attacked by insects, the hard wood (inner or fully developed wood) is seldom so affected. Elm, aspen, and all resinous woods are very seldom attacked by insects. Young wood which is full of sap and left with the bark on soon becomes quite worm-eaten, especially so the alder, birch, willow, and beech. The longer or shorter duration of wood depends more or less upon the following circumstances:—

(*a*) The conditions of growth. Wood from cold climates is generally more durable than that grown in warm climes. A poor soil produces, as a rule, a more durable and compact wood than does a soil rich in humus, and therefore containing also much moisture.

(*b*) The conditions in which the wood is placed greatly influence its duration. The warmer and moister the climate the more rapidly decomposition sets in; while a dry, cold climate materially aids the preservation of wood.

(*c*) The time of felling is of importance; wood cut down in winter is considered more durable than that felled in summer, as in the former season it contains much less sap. In many countries the forest laws enjoin the felling of trees only between November 15 and February 15.

Wood employed for building purposes in the country, and not exposed to either heat or moisture, is only likely to suffer from the ravages of insects; but if it is placed so that no draught of fresh air can reach it to prevent accumulation of products of decomposition, decay soon sets in, and the decomposing albuminous substances acting upon the fibre cause it to lose its tenacity and become a friable mass. Under the influence of moisture, fungi are developed upon the surface of the wood. These fungi are severally known as the "house fungi" (*Thetephora domestica* and *Boletus destructor*) and the clinging fungus (*Cerulius vastator*). They spread over the wood in a manner very similar to the growth of common fungi on soil. Their growth is greatly aided by moisture and by exclusion of light and fresh air. A chemical means of preventing such growths is found in the application to the wood of iron acetate, prepared from wood vinegar. Wood is often more injuriously affected when exposed to sea water, when it is attacked by a peculiar kind of mollusc known as the bore-worm (*Teredo navalis*). This creature is armed with a horned beak capable of piercing the hardest wood to a depth of 36 centimetres. These pests originally belonged to, and abound in great numbers in, the seas under the tropical clime, but they are also met with on the coasts of Holland and England.

Preservation of Wood in Particular.—The means usually adopted to prevent the destruction of wood by decay are the following:—

1. The elimination, as much as possible, of the water from the wood previously to its being employed.
2. The elimination of the constituents of the sap.
3. By keeping up a good circulation of air near the wood so as to prevent its suffocation, as it is termed.
4. By chemical alteration of the constituents of the sap.
5. By the gradual mineralisation of the wood, and thus the elimination of the organic matter.

1. *Drying Wood.*—Thoroughly dried wood remains for a long time unaltered while in a dry situation, more especially so when dried by so strong a heat that it becomes browned. When timber has to be put into a damp situation, it should, after having been well dried, be first coated with a suitable substance to prevent the moisture penetrating into the wood. This purpose is attained by coating the wood with linseed oil, so-called Stockholm tar, coal-tar creosote, and other hydrocarbons. Hutin and Boutigny adopt the following method to prevent the absorption of moisture by wood that is put into the ground:—The portion of the post or wood to be buried is first immersed in a vessel containing benzol, petroleum, photogen, &c., and when taken out is ignited and thus charred. When extinguished, the wood is put to a depth of from 3 to 6 centimetres into a mixture of pitch, tar, and asphalte, and next the entire piece of wood is thoroughly painted over with tar.

2. *Elimination of the Constituents of the Sap.*—The constituents of the sap are the chief cause of the decomposition of wood, and they should consequently be removed; many plans are adopted. The constituents of the sap can be eliminated from the felled tree by three methods:—

(1) By treatment with cold water, with which the wood must be thoroughly saturated to dissolve the constituents of the sap, which are removed when the wood is exposed to a stream of water. It is evident that with large timber a long time is necessary to ensure perfect saturation.

(2) By employing boiling water the sap is removed much more quickly and efficiently. The pieces of wood are placed in an iron vessel with water, and boiled. Large pieces of timber cannot be treated in this manner, but are immersed in a cistern in which the fluid is heated by means of steam. According to the thickness of the wood, the boiling occupies some six to twelve hours.

(3) By treatment with steam (steaming of wood)—the most effectual method of removing the constituents of the sap, the hygroscopicity of the wood thus treated being rendered much less, while the wood is far more fitted to resist the effects of weather. The apparatus employed in carrying out the method consists of a boiler for the generation of steam, and a cistern or steam chamber for the reception of the wood, this chamber being constructed of masonry and cement, of boiler-plate, or being simply a large and very wide iron pipe. In most cases a jet of steam is conveyed from the boiler to the steam chamber, where it penetrates the wood, and dissolves out the constituents of the sap, which, on being condensed, is allowed to run off. In the case of oak this fluid is of a black-brown colour; with mahogany, a brown-red; with linden wood, a red-yellow; with cherry-tree wood, a red; &c. The operation is finished when the outflowing water is no longer coloured. The steamed wood is dried in the air or in a drying-room; it loses from 5 to 10 per cent. in weight by the process, and becomes of a much darker colour. The steam is sometimes worked at a temperature of above 100°, but generally the contents of the steam chamber are maintained at from 60° to 70°. Towards the end of the operation some oil of coal-tar is introduced into the boiler, and is consequently carried over with the steam, impregnating the wood.

The removal of the sap can also be effected to some extent by means of mechanical pressure between a pair of iron rollers, which are gradually brought more closely together. Another method is by means of air pressure. Barlow employs for this purpose a metal case in which the wood is enclosed, and to one end of which an air pump is attached. Air being forced into the tube or case, the sap flows away at the end opposite to which the pump is attached. But both these methods are costly, and are not applicable in all cases.

3. *Air Drains.*—The construction of air drains or passages around woodwork to be preserved is, where the method is applicable, a great aid to the preservation of the wood. The consideration of the best means of effecting ventilation in this respect is

not a matter with which we can deal in this work. It is sufficient to say that, in many instances, the air channels are connected on the one hand with the open air, and on the other with the chimney.

4. *Chemical Alteration of the Constituents of the Sap.*—One of the most usual and most effective means of preventing the decomposition of wood is by producing a chemical change in the constituents of the sap, so that fermentation can no longer be set up. To this class belongs the well-known plan of protecting woodwork that is to be exposed to the action of the moisture of the earth by charring the wood, either by fire or by treatment with concentrated sulphuric acid, so that the wood is coated to a certain depth with a layer of charcoal, the charcoal acting as an antiseptic. The charring or carbonisation of the wood can be effected either with the help of a gas flame or the flame from a coal fire. The apparatus of De Lapparent, invented for this purpose, became very generally employed in 1866 at the dockyards of Cherbourg, Pola, and Dantzic. According to another method, the wood is impregnated throughout its whole mass with some substance that either enters into combination with the constituents of the sap, or so alters their properties as to prevent the setting up of decomposition. To this class belong the four following methods, these being the only ones that have met with any more extensive use.

(1) Kyan's preserving fluid is a solution of mercuric chloride of various degrees of concentration. In England a solution of 1 kilo. of corrosive sublimate in 80 to 100 litres of water is generally employed for railway sleepers. The timber is laid in a water-tight wooden trough containing the solution, where, according to its size, it remains a longer or shorter time. In Baden the wood remains in the kyanising solution, when it is to be impregnated to a depth of—

82 mm.,	for	4 days,
85 to 150	„	7 „
150 to 180	„	10 „
180 to 240	„	14 „
240 to 300	„	18 „

the solution consisting of 1 kilo. of sublimate to 200 litres of water. The prepared wood is washed with water, rubbed dry, and then placed in sheds free from exposure to rain and strong sunlight. The principal action of the mercuric chloride is to convert the albumen of the sap into an insoluble combination, capable of withstanding decomposition, while the bichloride becomes gradually reduced to mercurous chloride (calomel). A great objection to this method is the danger to which the carpenter or joiner who may afterwards shape the wood is exposed, the free chemicals acting upon his system through his hands, nostrils, and mouth. In England, wood to be varnished is seldom kyanised.

Erdmann remarks upon this plan of preserving wood that the interior of the log is still left in its original condition. To answer this objection the kyanising has been made more effective by placing the wood in a water-tight trough with the solution of sublimate, and, by a great pressure of air, thoroughly impregnating the wood. Kyanising by this method becomes, however, as expensive as any other impregnation method. Recently there has been substituted for the pure mercuric chloride a double salt of the formula $HgCl_2 + 2KCl$, obtained by decomposing a solution of carnallite with mercuric oxide.

(2) Burnett's (1840) patent fluid consists of 1 kilo. of zinc chloride dissolved in 90 litres of water. Wood treated with Burnett's fluid has been buried in the earth for five years without undergoing any change, while unprepared wood buried for the same length of time has been totally destroyed. Zinc chloride has been much used in Germany as an impregnating material. Besides this salt, copper sulphate and zinc acetate—zinc pyrolignite—(Scheden's method) have been employed. The action of

the copper and zinc salts may be explained by considering that the metallic oxides of the basic salt formed during seasoning separate, and combine with the colouring matter, tannic acid, resin, &c., of the wood to form an insoluble compound.

(3) Bethell's (1838) patented method consists in treatment under strong pressure with a mixture of tar, oil of tar, and carbolic acid, this mixture being known commercially by the name of *gallotin*. In and near London wood thus treated has remained eleven years in the earth without undergoing change; other pieces of timber so treated were subjected to the action of the sea for four years; and were still in good condition. Vohl employs for preservation peat and brown coal creosote; Leuchs uses paraffine. Such agents, however, render wood treated with them highly inflammable.

(4) Payne's method.—This includes two patents, the first having been taken out in 1841. Both are based on the impregnation of the wood—first with one salt, and next with another salt, which is capable of producing with the former a precipitate insoluble in water and in the sap of the tree. The first solution is usually one of iron sulphate or of alum; then follows a solution of calcium chloride or of soda. The wood to be impregnated is placed in a vessel from which the air is exhausted, the first solution being then admitted, and pressure subsequently applied. The first solution being removed, the second is admitted, and pressure again applied. It is necessary to dry the wood partially between the two impregnations. Payne's method, much used in England, possesses, moreover, the advantage of rendering the wood somewhat uninflammable. The same effect results with the methods of Buchner and Von Eichthal, who impregnate the wood with a solution of iron sulphate, and then with a water-glass solution, whereby the pores of the wood are filled with ferrous silicate. Ransome attains the same end by an impregnation with a water-glass solution and subsequent treatment with an acid. It is found that the treatment of wood according to the above methods is generally attended with good results. A method of impregnation with materials forming insoluble soaps, aluminium, and copper oleates, or those of other metals patented in 1862, has given some moderate results on the small scale.

5. *Mineralising Wood.*—When the terms mineralised, petrified, metallised, or incrusted are applied to wood, they mean that the wood has undergone impregnation with an inorganic substance, which has so filled the pores of the wood that it may be said to partake of the characteristics of a mineral substance. Suppose that the wood has become impregnated with iron sulphate and then exposed to the rain, the sulphate will be gradually dissolved out, in time leaving only a basic sulphate. By the researches of Strützki (1834), of Apelt in Jena, and of Kuhlmann (1859), the influence of iron oxide upon wood fibre has been rendered very clear. Wood impregnated with basic iron sulphate ceases to be wood after some time.

Boucherie's Method of Impregnation.—This method consists in the impregnation of the wood with the necessary substance, in a manner similar to the natural filling of the pores with sap; that is to say, the solution is introduced into the tree from its roots, and is thus made to take the place of the sap in all parts of the timber. When the tree is felled, the root end is placed in a solution of the salt (copper sulphate, iron acetate) and allowed to remain for some days; at the end of the required time the wood will have become completely impregnated with the salt. Occasionally this method is employed in colouring woods, colouring matter being used instead of, or as well as, the salt. The linden, beech, willow, elm, alder, and pear tree can be treated in this manner. The fir, oak, ash, poplar, and cherry tree do not, however, absorb the impregnating fluid sufficiently.

APPENDIX.

USEFUL TABLES.

THERMOMETRIC SCALES.

In this work temperatures, almost without exception, are given on the Centigrade scale, which takes the boiling-point of water at the ordinary atmospheric pressure at 100°, and its freezing-point at 0°. Where any other scale is used it is specially mentioned. The following rules will be useful for manufacturers who prefer to make use of the thermometer of Fahrenheit, or that of Réaumur.

To convert degrees Centigrade into degrees Fahrenheit:

If the temperature is above the freezing-point of water (0° C.), multiply by 9, divide by 5, and add 32 to the quotient.

If the temperature be below 0° C., but above − 18° C., multiply by 9, divide by 5, and subtract the result from 32.

If below − 18° C., multiply by 9, divide by 5, and subtract 32 from the result.

To convert degrees Fahrenheit into degrees Centigrade:

If above 32° F., subtract 32, multiply by 5, and divide by 9.

If below 32° F., but above 0° F., subtract the temperature from 32, multiply by 5, and divide by 9.

If below 0° F., add the temperature to 32, multiply by 5, and divide by 9.

The conversion of Réaumur's scale—in which the boiling-point of water is taken as 80°, and *vice versâ*—is effected in the same manner; the number 4 being used instead of 5 as a multiplier or divisor.

HYDROMETER TABLES.

For determining the specific gravity of liquids heavier than water the scale of Twaddell has been generally used.

For its conversion into direct specific gravity:

Multiply by 5, and add 1 to the product.

For converting specific gravity into Twaddell:

Subtract 1 and divide by 5.

The degree Tw. of any liquid shows its weight per gallon in pounds, if we prefix 1 and insert the decimal point before the last figure. Thus, hydrochloric acid = 32° Tw.; its weight, therefore, is 13·2 lbs. per gallon.

Some manufacturers, especially in the Liverpool district, use a hydrometer which shows direct specific gravity if we place 1 before its first figure. Thus a sample of hydrochloric acid of 32° Tw. will be on this scale 160°.

The scale of Baumé bears no simple relation to direct specific gravity; consequently its conversion into degrees Tw., and into direct specific gravity, can only be effected by means of tables, as follows:—

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
0	1·000	20	1·152	40	1·357	60	1·652
1	1·007	21	1·160	41	1·369	61	1·670
2	1.013	22	1·169	42	1·382	62	1·689
3	1·020	23	1·178	43	1·395	63	1·708
4	1·027	24	1·188	44	1·407	64	1·727
5	1·034	25	1·197	45	1·421	65	1·747
6	1·041	26	1·206	46	1·434	66	1·767
7	1·048	27	1·216	47	1·448	67	1·788
8	1·056	28	1·226	48	1·462	68	1·809
9	1·063	29	1·236	49	1·476	69	1·831
10	1·070	30	1·246	50	1·490	70	1·854
11	1·078	31	1·256	51	1·505	71	1·877
12	1·086	32	1·267	52	1·520	72	1·900
13	1·094	33	1·277	53	1·535	73	1·924
14	1·101	34	1·288	54	1·551	74	1·949
15	1·109	35	1·299	55	1·567	75	1·974
16	1·118	36	1·310	56	1·583	76	2·000
17	1·126	37	1·322	57	1·600		
18	1·134	38	1·333	58	1·617		
19	1·143	39	1·345	59	1·634		

For liquids lighter than water no determination can be effected with Twaddell's hydrometer. The scales used are those of Beck, Cartier, or Baumé's light instrument.

Deg.	Beck.	Cartier.		Baumé.	Deg.	Beck.	Cartier.		Baumé.
		a.	*b.*				*a.*	*b.*	
70	0·7083				35	0·8292	0·840	0·845	0·849
69	0·7112				34	0·8333	0·845	0·850	0·854
68	0·7142				33	0·8374	0·851	0·855	0·859
67	0·7173				32	0·8415	0·856	0·861	0·864
66	0·7203				31	0·8457	0·862	0·866	0·869
65	0·7234				30	0·8500	0·867	0·872	0·875
64	0·7265				29	0·8542	0·872	0·878	0·881
63	0·7296				28	0·8585	0·879	0·883	0·886
62	0·7328				27	0·8629	0·885	0·889	0·892
61	0·7359				26	0·8673	0·891	0·895	0·897
60	0·7391	...	...	0·744	25	0·8717	0·897	0·901	0·903
59	0·7423				24	0·8762	0·903	0·907	0·909
58	0·7456				23	0·8808	0·909	0·914	0·915
57	0·7489				22	0·8854	0·916	0·921	0·921
56	0·7522				21	0·8900	0·922	0·927	0·927
55	0·7556	...	..	0·763	20	0·8947	0·929	0·934	0·933
54	0·7589				19	0·8994	0·935	0·941	0·939
53	0·7623				18	0·9042	0·942	0·948	0·946
52	0·7658				17	0·9090	0·949	0·955	0·952
51	0·7692				16	0·9139	0·956	0·962	0·959
50	0·7727	...	...	0·784	15	0·9189	0·963	0·969	0·965
49	0·7763	...	...	0·786	14	0·9239	0·970	0·976	0·972
48	0·7799	...	...	0·792	13	0·9289	0·977	...	0·979
47	0·7834	...	...	0·795	12	0·9340	0·985	...	0·986
46	0·7871	...	...	0·799	11	0·9392	0·992	...	0·992
45	0·7907	...	...	0·803	10	0·9444	1·000	...	1·000
44	0·7944	0·794	...	0·807	9	0·9497			
43	0·7981	0·799	...	0·811	8	0·9550			
42	0·8618	0·804	...	0·816	7	0·9604			
41	0·8061	0·809	...	0·820	6	0·9659			
40	0·8095	0·814	...	0·824	5	0·9714			
39	0·8133	0·819	0·824	0·829	4	0·9770			
38	0·8173	0·825	0·829	0·834	3	0·9826			
37	0·8212	0·830	0·834	0·839	2	0·9883			
36	0·8252	0·835	0·839	0·844	1	0·9941			

The following scale is very often used for alcohol:—

Gay-Lussac's Alcoholometer (Alcoomètre) at 15°.

Degree.	Sp. Gr.	Degree.	Sp. Gr.	Degree.	Sp. Gr.	Degree.	Sp. Gr.
100	0·795	75	0·879	50	0·936	25	0·971
99	0·800	74	0·881	49	0·938	24	0·972
98	0·805	73	0·884	48	0·940	23	0·973
97	0·810	72	0·886	47	0·941	22	0·974
96	0·814	71	0·888	46	0·943	21	0·975
95	0·818	70	0·891	45	0·945	20	0·976
94	0·822	69	0·893	44	0·946	19	0·977
93	0·826	68	0·896	43	0·948	18	0·978
92	0·829	67	0·899	42	0·949	17	0·979
91	0·832	66	0·902	41	0·951	16	0·980
90	0·835	65	0·904	40	0·953	15	0·981
89	0·838	64	0·906	39	0·954	14	0·982
88	0·842	63	0·909	38	0·956	13	0·983
87	0·845	62	0·911	37	0·957	12	0·984
86	0·848	61	0·913	36	0·959	11	0·986
85	0·851	60	0·915	35	0·960	10	0·987
84	0·854	59	0·918	34	0·962	9	0·988
83	0·857	58	0·920	33	0·963	8	0·989
82	0·860	57	0·922	32	0·964	7	0·990
81	0·863	56	0·924	31	0·965	6	0·992
80	0·865	55	0·926	30	0·966	5	0·993
79	0·868	54	0·928	29	0·967	4	0·994
78	0·871	53	0·930	28	0·968	3	0·996
77	0·874	52	0·932	27	0·969	2	0·997
76	0·876	51	0·934	26	0·970	1	0·999

The weights and measures used in this book are given on the metric system. Their value in comparison with English weights and measures is as follows:

1 gramme = 15·4384 grains
1 decigramme = 1·5438 grain
1 centigramme = 0·1543 „
1 milligramme = 0·0154 „
1 micro-milligramme = 0·00001 „
1 kilogramme, generally abridged kilo. = 2·2054 lbs. avoirdupois
„ „ „ = 2·6803 lbs. troy
100 kilos. or metric quintal = 220·5486 lbs.
1000 kilos. or metric ton = 2205·486 lbs.

MEASURES OF CAPACITY.

1 cubic centimetre (generally written c.c.) = 15·438395 fluid grains (water)
1000 c.c. = 1 litre = 1·760773 imperial pint; or, = 0·2200967 imperial gallon
1 cubic metre = 1·308 cubic yard; or, = 35·3171 cubic feet
1 gallon of water (= 277·274 cubic inches) weighs 10 lbs.
224 gallons = 1 ton
1 cubic inch of water = 252·45 grains
„ „ mercury = 3425·25 „

MEASURES OF LENGTH.

1 metre	=	39·37079 inches = 3·2808992 feet = 1·093633 yard
1 millimetre	=	0·03937 inch
1 centimetre	=	0·393708 „
1 decimetre	=	3·937079 inches
1 inch	=	2·539954 centimetres
1 foot	=	3·0479449 decimetres
1 yard	=	0·91438348 metre
1 mile (1760 yards)	=	1609·3149 metres
1000 metres	=	1 kilometre

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